

**LASER EXCITED ATOMIC FLUORESCENCE SPECTROMETRY
AS A POWERFUL TOOL FOR ANALYTICAL APPLICATIONS
AND SPECTROSCOPIC STUDIES**

By

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Abstract of Dissertation Presented to the Graduate School
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Chairman: Prof. James D. Winefordner
Major Department: Chemistry

Laser-excited atomic fluorescence spectrometry (LEAFS) with a novel diffusive tube electrothermal atomizer (ETA) has been used for the study of atomization and diffusion processes and for the direct trace analysis of complex matrices.

A novel ETA was a graphite tube sealed by two graphite electrodes. A sample was introduced into the tube and the furnace assembly was heated. The vaporized sample diffused through the hot graphite and the atomic fraction of the vapor was excited by a tunable dye laser above the tube.

Temporal behavior of atomic fluorescence of Cu, Ag, and Ni atoms, diffused through the furnace tube, was studied at different temperatures; the values for activation energies

and diffusion coefficients were derived on the basis of the diffusion/vaporization kinetic model.

The femtogram/nanogram concentrations of silver were determined in coastal Atlantic water and soil samples. Use of the new ETA resulted in significant reduction of matrix interferences, ultra-low limits of detection, good accuracy and precision.

LEAFS coupled with laser ablation (LA) was studied in terms of its analytical and spectroscopic potential. Low concentrations of lead (0.15 ppm - 750 ppm) in metallic matrices (copper, brass, steel, and zinc) were measured in a low pressure argon atmosphere. No matrix effect was observed, providing a universal calibration curve for all samples. A limit of detection of 22 ppb (0.5 fg) was achieved. Also, the lifetime of the metastable $6p_1^2D$ level of lead was measured and found to be in good agreement with the literature data.

A simple open-air LA-LEAFS system was used for the determination of cobalt in solid matrices (graphite, soil, and steel). The fluorescence of cobalt was excited from a level which was already populated in the ablation plasma and was monitored at the Stokes-shifted wavelength. Detection limits in the ppb to ppm range and linearity over four orders of magnitude were achieved.

The resonance shadowgraph technique has been developed for time-resolved imaging of laser-produced plasmas. The shadowgraphs were obtained by igniting the plasma on the lead or tin surface and by illuminating the plasma by a laser tuned in resonance with a strong atomic transition. UV-photodecomposition of lead and tin clusters was visualized. The evolution of the plasmas was studied at different pressures of argon. A shock wave produced by the laser ablation was monitored and its speed was measured.

CHAPTER 1

LASER EXCITED ATOMIC FLUORESCENCE SPECTROMETRY IN ANALYTICAL CHEMISTRY: BASIC INFORMATION

Fundamentals

The method of atomic fluorescence spectrometry (AFS), which is based on selective absorption and following emission of light by atoms and molecules, has been known since the 1930s. Unfortunately, it was not widely used in an analytical practice until the 1970s due to the absence of powerful light sources and, consequently, due to a very low sensitivity as compared to other routinely used methods of spectral analysis (atomic absorption spectrometry (AAS), atomic emission in flames, arc and spark discharges, inductively coupled plasma (ICP), etc.). However, when powerful lasers, especially tunable dye lasers, became available, the method of laser excited atomic fluorescence spectrometry (LEAFS) was found to be one of the most sensitive and selective methods of atomic spectral analysis, allowing, in some cases, the determination of single atoms or molecules in the analytical volume [1,2].

The physical principle of LEAFS is based on the behavior of the atomic system in a strong laser field [3-7]. Two types of laser-induced fluorescence are usually used in experiments: resonance fluorescence, when the fluorescence light is monitored at the same wavelength as that of the laser excitation (two-level atomic scheme, Figure 1a), and the shifted or nonresonant fluorescence, when the fluorescence is collected at longer wavelength

relative to the excitation wavelength (three-level atomic scheme, Figure 1b). The latter is more favorable, allowing the elimination of strong laser scattering by using a simple spectral filter (a monochromator or an interference filter with a narrow bandpass).

As an example, consider a more general three-level atomic fluorescence. The rate equations which describe a time behavior of the levels populations N_i ($i=1,2,3$) are given by [3]

$$\begin{aligned} \frac{dN_1}{dt} &= -N_1 \rho_\nu B_{12} - N_2 (A_{21} + \rho_\nu B_{21} + R_{21}) + \frac{N_3}{\tau_{31}} \\ \frac{dN_2}{dt} &= N_1 \rho_\nu B_{12} - N_2 (A_{21} + \rho_\nu B_{21} + R_{21} + A_{23} + R_{23}) \\ \frac{dN_3}{dt} &= N_2 (A_{23} + R_{23}) - \frac{N_3}{\tau_{31}} \end{aligned} \quad (1),$$

where ρ_ν is the spectral energy density ($\text{J cm}^{-3} \text{ Hz}^{-1}$), A_{21} and A_{23} are the Einstein coefficients for spontaneous emission (s^{-1}), R_{21} and R_{23} are the probabilities of non-radiative (quenching) transitions (s^{-1}), B_{12} and B_{21} are the Einstein coefficients for stimulated emission ($\text{cm}^3 \text{ J}^{-1} \text{ s}^{-1} \text{ Hz}$), and τ_{31} is the lifetime of the level 3 (s).

The solution of differential equations (1) is usually expressed in terms of the population of the upper excited state (N_2) from which fluorescence photons are emitted. There are several factors which affect the final form of the solution and the magnitude of the fluorescence signal measured in the experiment; these factors include τ_{31} , the lifetime of the

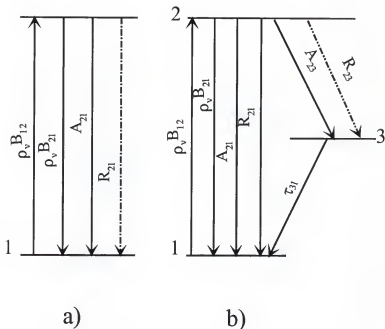


Figure 1. Diagrams of atomic levels commonly used in laser-induced atomic fluorescence experiments; a) two-level resonance fluorescence; b) three-level shifted fluorescence.

A_{21} and A_{23} are the Einstein coefficients for spontaneous emission from the level 2 to the levels 1 and 3, respectively; B_{12} and B_{21} are the Einstein coefficients for stimulated emission between the levels 1 and 2 caused by laser radiation with the spectral energy density ρ_v ; R_{21} and R_{23} are the probabilities of quenching transitions from the level 2 to the levels 1 and 3, respectively; and τ_{31} is the lifetime of the level 3 decaying to the level 1.

intermediate level 3, and τ_e , the time constant of the electronic data acquisition system. It is interesting to analyze the solution for the case of the metastable level 3 ($\tau_{31} \rightarrow \infty$) and for the case of the fast decaying level 3 ($\tau_{31} \rightarrow 0$). If the time constant τ_e is smaller than the width of the laser pulse, $\tau_e < \tau_{10}$, then the fluorescence signal, expressed in the number of fluorescence photons, is proportional to the population of level 2: $N_{ph} \propto N_2^{max}$ (amplitude registration). If the time constant τ_e is greater than the duration of the laser pulse, then the fluorescence signal is proportional to the integral $N_{ph} \propto \int N_2(t) dt$ (integral registration). Let us consider these possibilities sequentially.

Large τ_{31} , (metastable level 3), small τ_e (amplitude registration)

The approximate solution of (1) in its extreme point, i.e. $dN_2(t)/dt = 0$, is given by

$$N_{ph} \propto N_2^{max} \approx N_0 \frac{\rho_v B_{12}}{A_{12}^{\Sigma} + A_{23}^{\Sigma} + \rho_v B_{12} \epsilon} \quad (2),$$

where N_0 is the total number of atoms; $A_{21}^{\Sigma} = A_{21} + R_{21}$; $A_{23}^{\Sigma} = A_{23} + R_{23}$; and $\epsilon = 1 + g_1/g_2$.

At some critical laser spectral energy density, saturation of the atomic transition can occur, where the fluorescence from the upper level does not depend any more upon the laser energy density but only upon fundamental constants: statistical weights and Einstein coefficients. It is seen from (2), that N_2^{max} reaches the saturation value at

$$\rho_v \gg \frac{A_{21}^{\Sigma} A_{23}^{\Sigma}}{\epsilon B_{12}} = \frac{A_{21}^{\Sigma} A_{23}^{\Sigma}}{B_{12}^2 B_{21}} \quad (3),$$

where the relationship $B_{12}g_1 = B_{21}g_2$ between Einstein coefficients for stimulated emission has been used. Hence, the saturation value for N_2 becomes

$$N_2^{sat} = N_0 \frac{g_2}{g_1 + g_2} \quad (4),$$

that yields $N_2^{sat} = 1/2 N_0$ when $g_1 = g_2$.

Large τ_{31} , large τ_c (integral registration)

The number of fluorescence photons is now expressed by

$$N_{ph} = \int_0^{\tau_f} A_{23} N_2(t) dt \quad (5).$$

The solution of (5) is strongly dependent upon laser parameters (a spectral energy density, a pulse width), as well as upon parameters of an atomic system (transition probabilities, quenching constants). In first approximation, for a typical dye laser system, this solution is given by

$$N_{ph} \approx N_0 \frac{\rho_v B_{12} A_{23} \tau_f}{A_{21}^{\Sigma} + A_{23}^{\Sigma} + \rho_v B_{12} e} \quad (6).$$

At moderate laser intensities, the fluorescence increases linearly with the laser spectral energy density ρ_v ,

$$N_{ph} \approx N_0 A_{23} \tau_l \frac{\rho_v B_{12}}{A_{21} \Sigma A_{23}} \quad (7)$$

approaching the saturation value at high ρ ,

$$N_{ph} \approx N_0 \frac{A_{23} \tau_l}{\epsilon} \quad (8).$$

This solution has a limitation $A_{23} \tau_l / \epsilon < 1$ which follows from the numerical evaluation of the integral (5) (not shown here). Taking into consideration this condition, equation (8) acquires a clear physical sense: when level 3 is metastable, the atoms will undergo successive transitions 1-2-3 only once within the duration τ_l of the laser pulse. Therefore, in the presence of quenching ($R_{23} \neq 0$), only a fraction of the total number of atoms N_0 will contribute to the fluorescence at frequency ν_{23} .

Fast decay of the level 3 ($\tau_{31} \rightarrow 0$)

In this case, the three-level atomic scheme converges to the two-level scheme, providing $N_3(t) = 0$. The solution of the system (1) may be exactly the same as that expressed by Eqns 6 through 8 if the parameter $A_{23} \tau_l / \epsilon$ in (8) (the saturation mode) is much greater than 1, so that $N_{ph} \gg N_0$. This means that in a strong laser field, atoms undergo transitions between levels 1 and 2 without being retained in level 3 and emit fluorescence photons many times during the laser excitation pulse.

Finite lifetime τ_{31}

Again, in the first approximation, the solution of (1) is given by equation (6) and the limiting cases (7) and (8) are possible depending on the relationship between the parameter $\rho_e B_{12}$ and the values of A_{21} and A_{23} .

As one can see, in all cases considered, the situation can be realized in practice when the number of fluorescence photons emitted is nearly the same order of magnitude as or greater than the total number of atoms in the analytical volume. In terms of sensitivity, this provides a significant advantage of the method of laser-induced atomic fluorescence over all other methods where thermal sources of light are used (Figure 2). In the case of a thermal light source, the fluorescence signal, proportional to the population of a particular excited level, n_i , is determined by an exponential Boltzmann factor which reflects the distribution of atoms over all thermally excited energy levels. Typically, this factor is much less than unity providing that only a small fraction of light source atoms can contribute to the fluorescence signal. In contrast, for laser-induced fluorescence, the fluorescence signal is proportional to the population of only one selectively excited level and is determined by the ratio of statistical weights of levels which are involved into the radiative transition. This ratio can be close to unity providing that nearly all atoms present in the zone of interaction with the laser contribute to the fluorescence.

Instrumentation

The traditional laser atomic fluorescence spectrometer consists of three main components: an excitation source (a laser), an atomic reservoir (a graphite furnace, flame, ICP-plasma, etc.), and a system of data acquisition and processing.

The most popular source of the fluorescence excitation is a tunable dye laser which is usually pumped by an Nd:YAG laser [7], a nitrogen laser [8], or an excimer laser [9]. Recently, tunable diode lasers have also become widely used due to their low price, compactness and convenience in operating [10].

The system of atomization of samples is probably the weakest part of any laser atomic fluorescence spectrometer. It is impossible to design an ideal atom reservoir which could provide an efficiency of atomization close to unity and a freedom from spectral and chemical interferences. Therefore, a large variety of different atomizers are used in LEAFS depending on purposes pursued by researchers. Very popular atomizers are graphite furnaces or electrothermal atomizers (ETA) of various shape and size [7-12], especially those designed for AAS analysis. Some typical constructions of graphite furnaces used in LEAFS-ETA experiments are shown in Figure 3. Also, different types of flames (air-acetylene, air-hydrogen, etc.) [13-15], glow discharges in hollow cathode lamps [16-17], ICP-plasmas [18-19], and laser-induced plasmas [20-21] are used as atomic reservoirs.

A typical system for the detection of fluorescence consists of a collection optics, a spectral filter (usually, a monochromator or an interference filter) which transmits light only at the fluorescence wavelength, a photomultiplier tube (PMT), a gated integrator which opens the acquisition system for a short time (approximately equal to the width of the laser pulse), and a computer supplied with a software for a statistical data routine. An amplitude or an area of the fluorescence pulse, induced by a pulsed laser in a vapor of free atoms, is measured within the integrator time-gate. The sum of fluorescence signals over the time of atomization is usually taken as an analytical signal.

1. Thermal (flame, ICP, ...)



$$n_i = n_0 \frac{g_i}{Z} \exp\{-E_i/kT\}$$

Boltzman factor, $\exp\{-E_i/kT\}$

λ , nm	2000 K	4000 K	6000 K
200	10^{-36}	10^{-5}	10^{-5}
500	10^{-4}	10^{-4}	10^{-3}
700	10^{-3}	10^{-3}	10^{-2}

2. Laser Induced Fluorescence

a) Two-level scheme



b) Three-level scheme



$$n_2^{\text{sat}} = \frac{g_2}{(g_1 + g_2)} n_0$$

g-factor

$$g_1 = g_2 \quad g_1 = 9g_2$$

$$0.5 \quad 0.1$$

Figure 2. Comparison of a thermal light source with laser-induced fluorescence

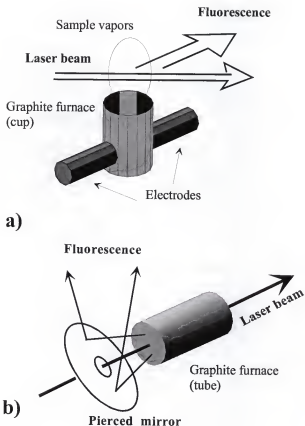


Figure 3. Graphite atomizers popular in LEAFS: a) an open type atomizer—a graphite cup; b) a closed type atomizer—a graphite tube

Analytical Performance of LEAFS

Traditionally, the potential of a new analytical method in comparison with other methods is determined by using calibration plots constructed on the basis of aqueous standards and by measuring limits of detection (LOD) of elements by the linear extrapolation of these plots to the level of triple standard deviation of the background signal.

LEAFS-ETA analysis of aqueous samples was carried out in references 3 and 7-12. The authors used a similar sampling routine: a small sample aliquot (10 μ L-50 μ L) was dosed into a graphite furnace, then dried and atomized at temperatures between 1200 $^{\circ}$ C and 3000 $^{\circ}$ C depending on the thermal-chemical properties of the element to be determined. An atmosphere of inert gas at normal or reduced pressure was used, or the sample was atomized in a vacuum, as in Bolshov et al. [7]. Dougherty and Prely [9] used LEAFS-ETA with a Zeeman background correction to obtain lower LODs and to improve an accuracy of the analysis relative to LEAFS-ETA without background correction. The atomizer (a graphite cup) was placed into a strong magnetic field modulated at a frequency of 60 Hz that caused atomic energy levels to be periodically split into Zeeman sub-levels. A pulsed dye laser was tuned in resonance with an atomic transition and operated at a repetition rate of 80 Hz. The fluorescence was excited by every second laser pulse at times when the field was off. When the field was on, no excitation occurred, and the background signal was measured. Cobalt was determined in aqueous standard solutions at the level of 0.3 pg (LOD) with a relative standard deviation of 0.13. Without the background correction, the LOD and the RSD were 0.7 pg and 0.3, respectively. Similar results for the determination of cobalt in aqueous

samples are reported in the literature [7, 11-12]; LODs in the range of 0.2 pg - 0.3 pg were achieved and RSDs ranged between 0.2 and 0.6.

Winefordner and Goforth [8] studied the analytical performance of LEAFS-ETA by using graphite furnaces of different shapes and size. Four elements (Al, Cu, Mo, and V) were determined in aqueous solutions. The use of a closed type atomizer, a graphite tube, yielded LODs of 100 pg, 8 pg, 100 pg, and $2 \cdot 10^5$ pg for Al, Cu, Mo, and V, respectively. The use of an open atomizer, a graphite cup, yielded LODs of 500 pg and 2 pg for Al and Cu, whereas Mo and V were not detected at all. The conclusion was made that graphite tube furnaces are advantageous over graphite cup atomizers, especially, for analysis of refractory materials. The same authors also studied how different furnace coatings (pyrolytic coating, a tantalum and a tantalum carbide foil alignment) and different inert atmospheres (argon, argon-hydrogen) affect the results of the LEAFS-ETA analysis [9]. The best LODs for six elements (Cu, Mn, Pt, Sn, In, and Li) in the range of 0.3 pg (In) - 400 pg (Li) were obtained by using a pyrolytically coated graphite tube furnace and an argon buffer gas at atmospheric pressure.

A high repetition rate (~ 10 kHz) copper vapor laser in a combination with ETA [12] or with a hollow cathode glow discharge [16] was used as a source for the fluorescence excitation. Such high repetition rate laser systems allow a significant increase in the probing efficiency as compared to commonly used low repetition rate (~ 10 Hz - 100 Hz) lasers. The limits of detection of 0.3 pg, 3 pg, 1 pg, and 0.03 pg were obtained [12] for Co, Ni, Fe, and Pb, respectively, and LODs as low as 0.015 pg for Pb and 2 pg for Ir were reported in Bolshov et al. [22].

The determination of 14 elements (Al, B, Ba, Ga, Mo, Pb, Si, Sn, Ti, Tl, V, Y, Zr, and U) was carried out by Human with coworkers [18] with the use of a ICP-LEAFS combination. The fluorescence could be excited either from atomic or from ionic energy levels that substantially enlarged a choice in finding the most convenient and free from spectral and chemical interferences transitions. The detection limits obtained were in the range of 0.4 ng/mL - 20 ng/mL, lower than average LODs achievable by the ICP-emission method. Theoretical aspects of the ICP-LEAFS combination are given in detail in Omenetto et al. [19]. Similar LODs for 19 elements (Ag, Al, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, Ti, Tl, and U) in the range of 0.08 ng/mL - 100 ng/mL were obtained by Weeks et al. [14] by using laser-induced fluorescence in flames.

LEAFS in an air-hydrogen flame with the use of a diode laser was demonstrated by Barber and colleagues [15]. The LOD of 0.2 ng/mL was obtained for Rb. A special cell containing rubidium vapor was used for the correction of the diode laser wavelength. An interesting application of LEAFS in flame was also reported by Simecosson et al. [23] who used photodissociation lasers for the determination of In and Tl in aqueous solutions. Photodissociation lasers are simple low pressure cells containing volatile halides of metals and pumped by an excimer laser. They are line sources with fixed wavelengths which are inherently tuned to atomic transitions of the same elements as those confined in active laser media. LODs obtained for Tl and In were 10 ng/mL and 80 ng/mL, respectively. The authors concluded that a fluorescence spectrometer on the basis of simple and cheap photodissociation lasers has a good potential for the sensitive determination of elements which form volatile halides.

Analysis of Real Objects

The utility of LEAFS as an analytical method has been demonstrated in numerous applications of LEAFS to the analysis of real objects: environmental, industrial, or biological.

The direct determination of antimony in environmental and biological samples by LEAFS-ETA was carried out by Enger et al. [24]. An intensified charge coupled device (ICCD) was used for continuous monitoring of a large spectral region. This allowed for the control and for the correction of various interfering background signals which appeared when samples of complex composition were analyzed. Measurements of the Sb content in drinking water, river water, marine sediments, human blood serum, and whole blood were performed in the concentration range from several $\mu\text{g/mL}$ to low pg/mL level with the accuracy less than 10 % RSD. The LEAFS-ETA technique was also successfully used for the direct determination of lead [25] and silver [26] in seawater ($\sim 1 \text{ ng/L}$ - 10 ng/L), iridium in industrial solutions (60 pg/mL - 1900 pg/mL) [22], lead in blood ($\sim 50 \text{ ng/mL}$ - 500 ng/mL) [27], metals (Cu, Fe, Mn, Pb, Sn, Tl) in air ($\sim 1 \text{ fg/m}^3$ - 1 ng/m^3) [28], etc.

Recently, the combination of LEAFS with laser ablation (LA) has become a popular method for the analysis of solids. In this method, very little or no sample preparation is needed that significantly reduces the chance for contamination due to handling. On the other hand, an extremely sensitive LEAFS method allows the determination of elements in laser plasmas at the part-per -billion (ppb) level of concentration. Quentmeier and colleagues [29] carried out the determination of four elements (Si, Mn, Mg, and Cr) in steel, copper, and aluminum. The plasma was induced by a Nd:YAG laser on the surface of solid targets, and

the fluorescence of two elements was excited simultaneously by two dye lasers. The internal standardization was proposed to account for matrix interferences and to obtain a universal calibration plot independent of matrix. Concentrations at a low part-per-million (ppm) range were detected. The LEAFS-LA method was also recently used for the determination of cobalt (low ppm level) in soil, steel, and graphite [30] and for the determination of lead in metallic matrices in the concentration range of 20 ppb - 700 ppm [31].

CHAPTER 2

NEW APPROACH IN LEAFS-ETA: DIFFUSIVE TUBE FURNACE

Introduction

One of the major problems, inherent in all analytical techniques using ETAs, is how to account for the various interferences which can exist when analyzing a particular matrix. These interferences are primarily due to an imperfection of the atomic cell design and usually include i) spectral interferences—black body radiation from the hot furnace, laser scattering from sample soot particles ejected into an analytical zone, molecular fluorescence from matrix concomitants; and ii) chemical interferences—solid phase reactions within the sample, sample or sample vapor interaction with the atomizer material, interaction between the analyte vapor and matrix gases within the furnace atmosphere (generation, decomposition, and transformation of various compounds) [32].

Many efforts have been made to improve the construction of the graphite furnace ETA and to optimize it for the analysis of the largest possible variety of real materials. In most early research on the LEAFS-ETA technique, open furnaces, such a graphite cup or a graphite rod, were used [10,33-34]. Since about 1985, commercially available graphite tube ETAs have been reported to be a much better choice for LEAFS-ETA than open graphite atomizers, because a graphite tube atomizer suffers less from diffusional losses and vapor-phase interferences. In addition, better detection limits for the

nonvolatile elements have been obtained [8-9,35-36]. Such graphite tube ETAs are widely used in atomic absorption spectrometry (AAS); past studies have indicated that there is no difference between the techniques of absorption and fluorescence in terms of the optimization of analytical methods because of the similarity of physical-chemical processes when the same furnace is used for both [37]. This leads to the conclusion that such electrothermal atomizers are equally well suited to both AAS and LEAFS.

During the last two decades, new type graphite furnaces, the furnaces with graphite filters, have been proposed for the analysis of liquids and solids by AAS [38-41]. The design of the furnaces was based on the separation of the atomization and analytical zones by means of a porous graphite filter which became transparent to vapors of some metals at high temperature. For example, the atomizer "capsule-in-flame" [38,39] has been applied for the analysis of powdered samples by AAS. The atomizer was a graphite cylinder (capsule) squeezed between two cylindrical graphite washers. The washers had holes to allow passage of a light beam along the capsule close to its surface. The air-acetylene burner was placed beneath the furnace. Powdered sample was introduced into the capsule cavity. The capsule was heated by an electric current and the sample vapor was released into the flame which was used to provide sufficiently high temperature in the analytical zone above the capsule. Such a furnace design allowed the elimination of soot particles which could be ejected into the analytical zone, the elimination of uncontrollable sample losses (that usually occur in open-cavity atomizers under pulse vaporization conditions) and the use of larger amounts of sample with respect to commercial ETA. It was also found that "capsule-in-flame" atomizer provides a relative freedom from chemical and spectral interferences.

Schmidt and Falk [40] carried out the direct AAS-determination of Ag, Cu, and Ni in biological and vegetation samples using a specially designed "ring chamber tube" with a sample chamber separated from the absorption volume. This "ring chamber tube" could be directly inserted into a commercial atomizer. These authors demonstrated the principal advantages of vapor filtration, such as suppression of background and interferences, and determined several elements in solid materials and found good agreement with certified values.

Several other types of closed-cavity atomizers for AAS have recently been reviewed by Katskov and coauthors [41] (see Figure 4). Also, a new design of a furnace with a graphite filter has been proposed. The furnace was a pyrolytic graphite tube with a spool-shaped insert made from porous graphite. The sample was injected into the ring cavity between the tube and the insert. After the pulse vaporization of the sample, the atomic vapor along with gaseous matrix components diffused through the porous insert into the analytical zone in the center of the graphite tube. In the course of the determination of Cd, Pb and Bi in the presence of excess matrices (NaCl or CuCl₂), Katskov et al. [41] discovered that molecular vapor entering the analytical zone was delayed relative to the atomic vapor. Further investigation [42] showed that this delay could be attributed to the formation of molecular intercalation compounds of different stoichiometry which were implanted into the graphite structure between crystalline layers. Enthalpies of formation were obtained on the basis of the kinetic analysis of different exponential portions of the signal which contributed to the total shape of the signal at different temperatures.

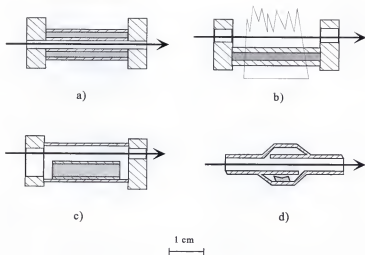


Figure 4. Atomizers with the sample vapor filtration for AAS; a) furnace with a ring cavity; b) capsule-in-flame; c) capsule-in-furnace; d) ring chamber tube. Shaded areas represent sampling volumes; arrows represent light source beams.

Therefore, one can conclude that the use of a diffusive media in an ETA, made of a porous graphite (or, perhaps, other porous material), provides a high-temperature separation of matrix components and leads to minimization of spectral and chemical interferences.

Furnace Design

The design of the furnace is shown in Figure 5. The graphite tube (1), which served as the porous filter, was made from a carbon electrode of density 1.65 g/cm^3 (Type F, ultra pure, Ultra Carbon Corporation, Bay City, Michigan, USA) used for spectral emission analysis. The length and the external diameter of the tube were 22 mm and 6 mm, respectively. The diameter of the inner channel was 3.5 mm in the central part of the tube and was enlarged to 4.6 mm toward the tube ends at a distance of 3 mm from each end.

The graphite tube was held between two spring-loaded graphite electrodes (3,4) of 4.5 mm in diameter with rounded tips. The electrodes firmly held the tube providing a good seal of the inner tube channel and good electric contact between the tube and the electrodes. One of the electrodes (3) had an insert in the form of a smaller diameter (3 mm) graphite rod (2) which had a hollow for a sample. This electrode could slide back and forth in a stainless steel mount (5). To load a sample, the electrode was pulled out to the position where the rod hollow was between the mount and the tube. The maximum acceptable volume for a single dosing was about 50 μL .

The furnace assembly was constructed from a commercial carbon rod atomizer CRA-90 (Varian Techtron, Springvale, Australia). The atomizer, initially designed for AAS,

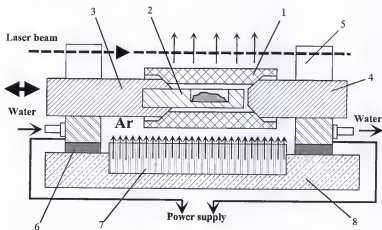


Figure 5. Furnace with graphite filter: 1, porous graphite tube; 2, graphite rod with a sampling boat; 3-4, electrodes; 5, steel mount; 6, insulator; 7, shim chimney for the laminar argon flow supply; 8, stainless steel platform.

was modified to suit the purposes of the LEAFS experiment. Two rectangular windows were cut in the stainless steel electrode mounts to allow passage of a laser beam along the graphite tube furnace close to its surface. The CRA-90 control unit was also modified to provide an atomization time up to 10 min, instead of a maximum of 5 s initially specified. The furnace assembly was inclosed in a gas-tight chamber filled with argon at one atmosphere pressure during the atomic fluorescence measurements.

Experimental Set-Up

The LEAFS-ETA instrumentation with a diffusive tube furnace is shown in Figure 6. The components of the experimental set-up are listed in Table 1. The 308 nm line of a xenon-chloride excimer laser was used to pump a Cresyl Violet 670 dye laser at a repetition rate of 25 Hz. Stray light from the excimer laser incident on a photodiode was used to trigger a boxcar integrator. The dye laser output was frequency doubled by a KDP crystal to produce a UV excitation wavelength which was directed through a quartz window into an atomizer chamber and was used to excite atoms generated above the diffusive tube furnace. Tuning the laser to the wavelength of the atomic transition of an element of interest was carried out with a second spectrometric system consisting of an air-acetylene flame in which the element stock solution was nebulized, a monochromator, a photomultiplier tube (PMT), and an oscilloscope with a 300 MHz bandwidth. The fluorescence signal from atoms in the flame was visually monitored on the oscilloscope screen.

The furnace (Fig.5) was enclosed within an atomizer chamber which has been designed to be compatible with an argon atmosphere at controlled pressure. The

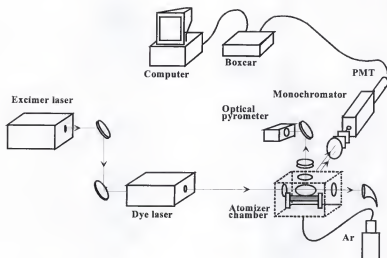


Figure 6. Schematic of the experimental set-up

Table 1. Components of the experimental system

Component/Model	Manufacturer
Excimer laser/LPX100	Lambda Physic, Gottingen, Germany
Dye laser/EPD-330	Lumonics, Ottawa, Ontario, Canada
Frequency doubler/KDP	Interactive Radiation, Northvale, NJ, USA
Monochromator/Digichrom	CVI Laser, Albuquerque, NM, USA
PMT/R928	Hamamatsu Photonics K.K., Toyooka Vill, Japan
Boxcar integrator/SR265	Stanford Research Systems, Palo Alto, CA, USA
Amplifier/SR440	Stanford Research Systems, Palo Alto, CA, USA
Atomizer/CRA-90	Varian Techtron, Springvale, Australia
Infrared thermometer/OS3709	OMEGA Engineering, Stamford, CT, USA
Computer/IBM/PC386	CLUB American Technologies, INC., Fremont, CA, USA
Software/Stanford	Metagraphics Software Corp., Copyright 1988 by Stanford Research Systems, Palo Alto, Ca, USA

chamber contained two parts: the steel platform, on which the furnace assembly was mounted and a cubic aluminum top with quartz windows on each face. A laminar argon flow was supplied from beneath the furnace. The distance between the laser beam and the furnace surface was 4 mm. The fluorescence emitted by excited atoms was detected at 90° to the direction of the laser beam. To collect the fluorescence from the entire excitation pathlength (~ 2 cm) and, hence, to increase the collection efficiency, the monochromator was rotated on its side (90°) so that the entrance slit was parallel to the laser beam. A 0.24 m focal length monochromator with an effective aperture of $f/3.9$, blazed at 250 nm, was used. Two biconvex lenses (51 mm diameter, 76 mm focal length) projected a 1:1 image of the analytical volume on the monochromator slit. The optical system was aligned by using emission from an electrically heated tungsten filament, positioned on the excitation axis. The thin tantalum foil diaphragm was placed in front of the furnace at a distance of 10 mm to block thermal blackbody radiation emitted by the hot furnace in the horizontal direction. The blackbody radiation in the vertical direction was detected by a photodiode, calibrated by an infrared thermometer, to monitor the temperature of the furnace surface.

The detection system included a PMT, a voltage amplifier with a gain of ten, and a boxcar integrator with a gate width of 20 ns. To keep the PMT in the linear range, the fluorescence signal was attenuated by a set of colored glass filters which were calibrated at the excitation and fluorescence wavelengths. The data were acquired and manipulated with a personal computer which recorded the fluorescence signal as a function of atomization time.

CHAPTER 3

HIGH TEMPERATURE DIFFUSION THROUGH POROUS GRAPHITE

Objectives

In spite of extremely high sensitivity of LEAFS, it has one serious limitation. LEAFS is essentially a single-element technique. This is due to the nature of the excitation source, a laser: it is impossible to obtain highly intense light in a large spectral range but only within a narrow wavelength window (~ 0.01 nm) selected by a laser cavity from a spectral band (~ 20 nm) of a laser dye. The high cost of good and reliable laser systems (dye laser pumped by an excimer or Nd:YAG lasers) makes their application unpractical for a determination of only one element in time. Therefore, up to this date, LEAFS instruments are not commercialized and are not used in routine analysis.

However, there are some ways to overcome this drawback. Tunable dye lasers which are usually used in LEAFS can be tuned to different wavelengths within the generation range of the dye. If several elements have transitions within the same spectral range then they can be sequentially excited by the laser. Unfortunately, it takes some time to tune the laser to the chosen wavelength (hardware limitation). This time ranges from seconds for lasers with diffraction gratings to milliseconds for lasers with opto-acoustic wavelength selectors. Nevertheless, if a construction and variable parameters (temperature, ramp rate)

of the atomizer are chosen in such a way to allow the sequential release of atoms into the analytical zone (a zone where free atoms interact with laser light), similar to chromatography, then the time between the appearance of two elements in the analytical zone could be made long enough to provide tuning the laser from one wavelength to another. This would increase the performance of LEAFS-ETA and, instead of the determination of only one element in one atomization cycle, one could sequentially determine several elements in the same sample and the same atomization run. To do this, knowing the diffusion coefficients and their temperature dependence is essential.

Therefore, evaluation of diffusion coefficients of elements in a graphite atomizer was a part of this work. The study presented in this chapter attempts to provide some new data on processes involved in the diffusive graphite tube ETA by using a kinetic approach to examine the diffusion of three elements (Ag, Cu, and Ni) through hot graphite. The elements copper, silver and nickel were chosen for the diffusion study for the following reasons. First, copper and silver have low melting points (1083 °C and 962 °C, respectively) and the formation of atoms in the analytical zone can be easily measured over a wide temperature range. Second, copper and silver do not form stable carbides. Third, the atomization of these three elements in graphite ETAs has already been extensively studied, and the abundance of experimental data which have been accumulated in the literature is useful for comparison with our results. Finally, all three elements have strong atomic transitions within the spectral range of the dye laser available for our experiment.

Theoretical Model

The problem of diffusion, complicated by vaporization and chemical interaction, may be solved by considering the generalized diffusion equation [43,44]

$$\frac{dn}{dt} = D \frac{\partial^2 n}{\partial x^2} - kn \quad (9)$$

where n is the number density of atoms in the substrate (cm^{-3}), t (s) the time, x (cm) the coordinate along the diffusion path, D (cm^2/s) the diffusion coefficient and k (s^{-1}) the first-order reaction rate constant. Unfortunately, this equation can be solved analytically only for a very few special cases. Therefore, the use of the semi-empirical models, which will be described below, is often the only way to solve the problem.

When solid state diffusion, vaporization, or chemical reactions leading to the formation of free atoms in the analytical zone are considered as successive phenomena, the kinetics of the process are determined by the stage with the largest rate constant. The rate equation for the change in amount of analyte atoms, N , in the analytical zone can be written in the form of a differential equation [45]:

$$\frac{dN(t)}{dt} = \left(\frac{dN}{dt} \right)_{in} - \left(\frac{dN}{dt} \right)_{out} \quad (10)$$

where the two terms on the righthand side express the rate of supply and the rate of removal of the atoms. The number of atoms in the analytical zone can also be expressed in terms of an integral equation [45-46] which is more convenient for practical use:

$$N(t) = \int_0^t S(t')R(t-t')dt' \quad (11)$$

where $S(t) = (dN/dt)_{in}$ is the supply rate of the atoms, and $R(t)$ is the normalized response of the system ($R_{max} = 1$) to the supply of an infinitely rapid pulse of atoms. If the removal function $R(t)$ is very rapid in comparison with the supply function, then the convolution integral in (11) can be transformed into the form:

$$N(t) = S(t) \int_0^t R(t)dt = S(t)\tau_R \quad (12)$$

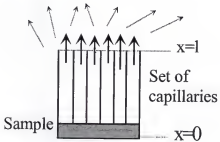
where τ_R is the equivalent time constant of the removal function. Thus, the temporal behavior of $N(t)$ (or the shape of the absorption or the fluorescence signal) reflects the time dependence of the supply function. In many publications on AAS [45-50], it has been shown that the supply function can be adequately described by first-order kinetics. Such kinetics can be attributed to specific processes under chosen experimental conditions: solid or gas phase reactions, evaporation, thermal decomposition, adsorption, and surface and bulk diffusion. The same information in terms of rate constants can be obtained by analyzing either the initial or the decay portions of the analytical signal. It was shown [47], however, that the latter is more advantageous because it is easier to attain an isothermal environment for the furnace and to make the results independent of temperature-sensitive parameters such as the atom residence time in the analytical zone and spectral line characteristics [51].

The main (if not sole) available parameter, related to the atomization mechanism, which can be obtained from direct measurements of the absorbance or the fluorescence signals, is an activation energy. This energy can then be compared with tabulated data of thermodynamic constants to determine which of the possible mechanisms of sample transformation is more likely. However, the principal difficulty in the study of the atomization mechanism by AAS or LEAFS is the impossibility of creating experimental conditions favoring one process over all others. All the processes are interrelated and often occur simultaneously. This is usually reflected by the shape of the Arrhenius plot (logarithm of a measured quantity such as rate constant, absorbance, fluorescence, vs inverse temperature) in the form of breaks and irregularities which have been observed for many elements [45,48,52].

In some early studies of the mechanism of atom formation in the ETA [48,52], solid-state diffusion through the porous wall of the furnace was considered as a pure loss process. This type of loss was regarded as having a minimum influence on the removal function (see Eqn 11) compared to the diffusion in the gaseous phase. Nevertheless, Smets [48] pointed out that grain boundary diffusion in porous graphite could strongly affect the atom supply and the kinetic behavior of the analytical signal. This could result in the temporal shape of the signal being markedly different from that obtained after evaporation from an ideal, impermeable surface.

A macrokinetic theory, developed to account for the surface diffusion in graphite ETAs and to explain the appearance of breaks and inflections in the Arrhenius plots, was first proposed by L'vov et al. [53] (see Figure 7). The theory described surface diffusion in

Diffusion (D) + Vaporization (V)



a) Low temperatures: $D > V$

$$E_a = H_{\text{vapor}}$$

b) Moderate temperatures: $V \sim D$

$$E_a = 1/2 (Q_{\text{dif}} + H_{\text{vapor}})$$

Figure 7. Macrokinetic model of diffusion

porous graphite accompanied by vaporization. The model of a porous body was represented as a set of equal cylindrical capillaries of radius ρ . The sample mass was taken to be initially located at some depth below the surface. Two limiting cases were considered. First, if the rate of diffusional transport is much larger than that of vaporization (the authors denoted this as "effusional kinetics"), then the supply function S can be expressed in the form

$$S = \pi \rho^2 q k \quad (13),$$

where q is the number of atoms per unit area and k is a vaporization constant (s^{-1}). In the second case, when vaporization is very fast compared to diffusion ("diffusional kinetics"), the supply function can be written

$$S = 2\pi\rho\sqrt{Dk} \quad (14)$$

where D is the surface diffusion coefficient (cm^2/s). Taking into account the Arrhenius-like temperature dependence of both k and D ,

$$k = k_0 \exp\left(\frac{-\Delta H}{RT}\right) \quad \text{and} \quad D = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (15)$$

where ΔH is the heat of vaporization, Q the diffusion activation energy, R , the gas constant, and k_0 (s^{-1}) and D_0 (cm^2/s) - preexponential factors, one can obtain the values for activation energy from (13 -15)

$$E_a = \Delta H \quad \text{and} \quad E_a = \frac{1}{2}(Q + \Delta H) \quad (16)$$

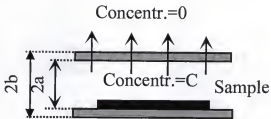
for the two cases under consideration. Therefore, the Arrhenius plot will show different slopes at different temperature regions, only if $\Delta H \neq Q$. For most of the metals which are usually determined by AAS or LEAFS, the heat of vaporization ΔH is larger than Q . The typical value for Q is ~ 80 kJ/mol (as was shown in reference [54] for 12 elements), and ΔH typically lies within the range of 100–400 kJ/mol. In the high temperature region, atomization is usually driven by diffusional kinetics, i.e., competitive diffusion/vaporization process, whereas at lower temperatures effusional kinetics are dominant and the heat of vaporization determines a time-behavior of the supply function. The proposed theory [53] was confirmed using as an example the atomization of copper in a graphite ETA. The data obtained, $E_a = \Delta H = 317$ kJ/mol for the low temperature region ($T \leq 1400$ K) and $E_a = 1/2(\Delta H + Q) = 203$ kJ/mol for the high temperature region ($T \geq 1400$ K) were in excellent agreement with tabulated values ($\Delta H_{1400} = 317$ kJ/mol, $Q = 78$ kJ/mol, $1/2(\Delta H + Q) = 198$ kJ/mol).

It is worth mentioning in this relation, that the enthalpy ΔH should be considered in a broader context than only as a heat of vaporization. It can also be attributed, for example, to the enthalpy of a specific chemical process or to the bonding energy of a metallic dimer, depending on which process is rate-determining under the conditions chosen. For example, the values for the activation energy in the range of ~ 75 –95 kJ/mol were reported by Smets [48] for different physical chemical transformations of copper oxide.

If we extend our considerations to the range of even higher temperatures, where the condensed phase can barely exist in a porous medium (graphite), then the mechanism of the formation of atoms in the analytical zone, beyond the diffusive layer, can be considered as a permeation of an atomic (or molecular) vapor through the membrane. This permeation may be a simple flow through a capillary but we shall exclude this case from consideration and deal only with true diffusion processes. Contrary to gaseous flow, which does not show very pronounced differences for different gases, true diffusion is a highly specific process which depends on the solubility and mobility of atoms or molecules in the solid [55]. In this case, the model proposed by L'vov et al. [53], which represents a porous body as a set of capillaries, is only approximately valid. A traditional approach to the high-temperature diffusion problem seems to be more relevant.

A simple model of diffusion of an atomic vapor through a membrane-like graphite cylinder was proposed by Katskov [51] (Figure 8). In the experiment, he used a 2-step ETA with a separate vaporizer and a pyrolytic graphite furnace. A spool-like porous graphite filter was tightly inserted into the furnace. After pulsed sample vaporization, vapors were quickly injected into the furnace between two concentric cylinders, forming the furnace and the filter walls, and then diffused through the filter partition to the analytical zone. The absorbance was measured in the center of the furnace. The temporal profile of the signal reflected the time-dependence of the supply function $S(t)$ which was a flux of analyte atoms through the surface of the graphite filter. If the rate of change in concentration due to diffusion is proportional to the concentration in the filter body, one can write

Diffusion



High temperatures

$$E_a = Q_{\text{dif}}$$

$$\text{Rate constant: } r = 4D[2a^2 \ln(a/b) + b^2 - a^2]^{-1}$$

$$\text{Arrhenius eqn: } D = D_0 \exp[-Q/RT]$$

Figure 8. Diffusion out of the hollow cylinder

$$S(t) = -\frac{dN_F}{dt} = -kN_F \quad (17)$$

where N_F is the number of atoms in the filter body and the parameter k (s^{-1}) is the diffusion rate of atoms in graphite. If the diffusion is not complicated by other physical chemical processes, the flux of atoms through the surface of the graphite filter is given by the Fick's diffusion equation:

$$S(t) = -Ds \nabla n \quad (18),$$

where D (cm^2/s) is the diffusion coefficient, s (cm^2) is the surface area, and ∇n is the gradient of the atomic number density n (cm^{-3}) in the substrate material. Under the experimental conditions, when the appearance time of the analytical signal is at least 10 to 20 times shorter than the duration of the whole signal at any chosen temperature, the diffusion can be considered as quasi-stationary, although neither the concentration nor the concentration gradient are constant. The solution of the steady-state diffusion equation for the hollow cylinder is well known [56]:

$$n = A + B \log r \quad (19)$$

where A and B are constants to be determined from the boundary conditions at $r=a$, $r=b$ (a and b are inner and outer radii of the cylinder, respectively). If the inner surface $r=a$ is kept

at almost constant concentration $n(a)$, and $r=b$ at zero concentration (the reverse conditions of Katskov's experiment, but not essentially changing the picture), then

$$n(r) = n(a) \frac{\ln \frac{b}{r}}{\ln \frac{b}{a}} \quad (20)$$

Integrating (20), one finds the total number of atoms in the cylinder body

$$N(t) = \int_a^b 2\pi r n(r) \cdot \frac{\pi n(a)}{2 \ln \frac{b}{a}} [2a^2 \ln \frac{a}{b} + b^2 - a^2] \cdot dr \quad (21)$$

Combining (17) and (18), and taking into account the surface area of the particle source $S=2\pi Lb$, where L is the length of the furnace, one finally obtains

$$k = 4D [2a^2 \ln \frac{a}{b} + b^2 - a^2]^{-1} \cdot \quad (22)$$

The diffusion coefficient D can now be easily determined by measuring the rate constant k from the decay portion of the analytical signal. The temperature dependence of D is expressed by the Arrhenius equation:

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (23)$$

where D_0 is the preexponential factor and Q is the diffusion activation energy. Measuring k at different temperatures and plotting $\log k$ vs $1/T$, one can find the values for Q and D_0 .

Now, it can be easily seen that for a process driven by pure diffusion, the total activation energy E_a is equal to the diffusion activation energy Q . The proposed model, however, does not explain the inflections on the Arrhenius plot and does not show from which part of the plot the diffusion coefficient can be obtained. The Arrhenius plot for silver, represented by the author [51], showed a break at a temperature of ~ 1560 K. The value of E_a of 235 kJ/mol, obtained for the low-temperature region (below 1560 K), closely coincided with the heat of vaporization of silver, although condensation with a consequent re-vaporization has not been considered. At higher temperatures ($T > 1560$ K), $E_a = 103$ kJ/mol and chemical interaction has been assumed.

It seems to be a reasonable suggestion, that even in the 2-step ETA, with independent pulse vaporization, condensation and re-vaporization of the sample take place, especially, if the temperature of the preheated furnace is far below the boiling point of the analyte, as is true for silver at $T < 1560$ K (B.P. 2485 K). Therefore, the diffusion equation should also include a term to account for vaporization. On the other hand, the model proposed by L'vov explains the behavior of the Arrhenius plot quite satisfactorily and gives a value of the activation energy for the low-temperature range equal to the heat of vaporization. Also, for the moderate-temperature region, the theoretical predictions of E_a coincided with the observed values within a range of uncertainty $\pm 20\%$ (such a comparison is given in reference [53] for 12 elements). However, in the range of very high temperatures, where the condensed phase of the analyte no longer exists and in the absence of chemical interaction,

the diffusion model of Katskov [51] seems to be relevant. Therefore, for some elements, satisfying these conditions, one can expect the appearance of a portion in the Arrhenius plot with a slope proportional to the diffusion activation energy Q .

Experimental Procedure

The experimental set-up (see Figure 6) was described in detail in Chapter 2. Key features of the experimental routine are given here. A sample (a 10 μL aliquot of a 100 ppm standard solution of Cu, Ag, or Ni) was loaded into the sampling hollow of the diffusive tube furnace (Fig. 5). After the sample was dried in air by a radiant heat projector, the insert was placed into the center of the graphite tube which was then sealed by the electrodes and heated. A five-step heating program was applied for all three elements. The program included a charring step (10 s, 700 $^{\circ}\text{C}$), a rapid, brief initial atomization step (1 s, 2000-2300 $^{\circ}\text{C}$), a relaxation step (5 s, 1000-1300 $^{\circ}\text{C}$), an atomization step (10-300 s, 1100-2300 $^{\circ}\text{C}$), and a cleaning step (2 s, 2300 $^{\circ}\text{C}$). The reason for using two extra steps (initial atomization and relaxation) with respect to the traditional temperature program (drying-charing-atomizing-cleaning), was to provide a pulse injection of the sample vapor into the furnace cavity, prior to diffusion through the graphite partition into the analytical zone. Alternately, if partial condensation takes place at the temperature of the relaxation step, this step serves to create a uniform distribution (ideally, close to a monolayer). In this case, the second pulse atomization is facilitated because the furnace is already pre-heated to a significant temperature, above the melting point of the element under study, and the condensed phase is distributed as a thin layer on the inner surfaces of the furnace.

To excite the fluorescence of the element under study, the laser beam was directed along the graphite tube surface so that no gap remained between the beam and the tube surface. The wavelengths of 324.8 nm/510.6 nm, 328.1 nm/338.3 nm, and 322.2 nm/361.9 nm were used for the fluorescence excitation/collection for Cu, Ag, and Ni, respectively .

Fluorescence vs time profiles for each of the elements studied were stored in the computer by using the program "Stanford" (Megagraphics Software Corp., Stanford Research systems, Palo Alto CA, USA). At least three parallel measurements were performed at each temperature. The rate constants (k) were measured from the decay portions of the fluorescence signal when a constant temperature was established in the furnace shortly after the signal maximum was reached. Under the assumption of first-order kinetics, the exponential function $y = a + b \exp[-kt]$ was fitted to the decaying part of the signal by using the same software ("Stanford") utilizing a least-square method. Then the plot of the logarithm of the rate constant vs the reciprocal of the absolute temperature (the Arrhenius plot) was drawn and the activation energy, E_a , was evaluated from the slope of this plot. The value of the pre-exponential factor k_0 (and D_0 through the Eqns 22,23) was obtained from the intersection of a high temperature fragment of the Arrhenius plot with the log k -axis at $1/T \rightarrow 0$ ($T \rightarrow \infty$). The experimental error was propagated from k to D by using Eqn 22.

Results

Atomic-fluorescence vs time profiles were measured within the temperature range of 1400 K - 2600 K. The absolute amount of each analyte, introduced into the furnace as the nitrate, was 1 μg . This relatively large amount was used to provide quasi-stationary conditions for diffusion, so that the atomic number density at the inner wall of the porous

graphite cylinder could be almost constant during the measurements. It was possible, however, that the fluorescence signal from such a large amount of analyte could become non-linear due to self-absorption of the fluorescence light by the dense atomic vapor in the analytical zone. To avoid this effect and also to provide for a fast removal of the atomic vapor from the space beside the furnace (so that the number density of the analyte atoms was near zero at the outer furnace wall), a rapid upward flow of argon gas at 4 L/min was used. Additionally, the proportionality between the amount of the sample and the analytical signal was checked. The calibration curves, shown in Figure 9, indicate that the fluorescence response was proportional to the absolute amount of each element over a range of 6 orders of magnitude, up to the value of 1 μg .

Special care was taken to measure rate constants under isothermal conditions. The analytical zone, from which the fluorescence radiation was collected, was restricted in size by a set of diaphragms (3x3 mm in the longitude direction, equal to the laser cross-section, and 2 mm in the perpendicular direction) to insure the observation of diffusion from only the isothermal part of the furnace. Temperature measurements showed, that the temperature was constant only in the central part of the furnace, at a distance of 4-5 mm from the center, and was 50-150 $^{\circ}\text{C}$ lower near the furnace ends, depending on the magnitude of the final temperature of atomization. The typical distribution of the atomic vapor above the surface of the graphite filter is shown in Figure 10. These data were obtained when a pure copper sample was vaporized at a temperature of 1800 $^{\circ}\text{C}$. It is seen from Figure 10 that the density of the atomic vapor above the furnace wall can be quite satisfactory approximated by a step-function with a width of about 5 mm. Therefore, the observation of a 2 mm segment of the

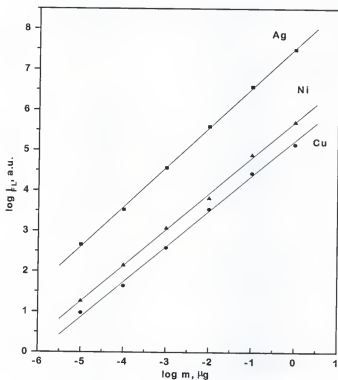


Figure 9. Calibration plots for Cu, Ag and Ni obtained in the diffusive tube ETA by using aqueous standards. m is the mass of each analyte (Cu, Ag, or Ni) in the 10 μL sample aliquot; the solid lines represent a linear regression fit to the experimental points.

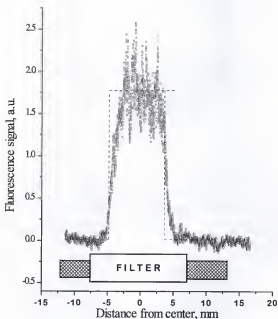


Figure 10. Spatial distribution of fluorescence signal and copper atoms above the graphite tube with a constant atomic vapor flow.

analytical zone allowed us to avoid the small non-uniformity of the temperature along the furnace wall.

Copper

In the experiment, rate constants for the atomization of copper were obtained over a temperature range of 1550-2600 K. The upper limit of this range was equal to the maximum temperature which could be obtained with our particular ETA unit. The lower limit was determined by the uncertainty in the results at temperatures below 1500 K. In this case, the total time of the atomization exceeded 300 s and signal shapes for consecutive runs could differ significantly. This resulted in errors of up to 100%, when an exponential fit was applied to such a slowly decaying portion of the signal. Therefore, the experiment was not run below a temperature of 1500 K and the results were only considered as satisfactory if they fell within an uncertainty range of $\pm 30\%$.

Figure 11 shows the Arrhenius plot for copper which was constructed on the basis of the two sets of data. The upper part of the plot was constructed from data obtained in a temperature region of 1550-2600 K by using a LEAFS-ETA technique (circles, connected by the solid line). The lower part (crosses, connected by the dashed line) represents some data, extracted from L'vov et al. [53], which have been obtained in the temperature region of 1250-1600 K by using an AAS-ETA technique and a quasistatic method for the evaluation of the parameter k . This method was similar to ours and also utilized the decay portion of the analytical signal. It can be seen, that the plot consists of three linear parts with two inflection points: at ~ 1770 K and at ~ 1380 K. In the middle part, corresponding to the temperature region of 1380-1770 K, the two linear plots, obtained from two different

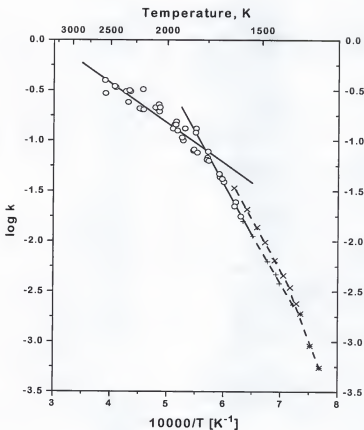


Figure 11. Arrhenius plot for copper constructed on the basis of the two sets of data: obtained in this experiment (circles connected by the solid line) and extracted from L'vov et al. [53] (crosses and stars connected by the dashed lines). The lines represent a linear regression fit to the experimental points in different temperature regions.

experimental systems, show nearly the same slopes. The complete coincidence of the plot from L'vov et al. [53] with our data should be considered as accidental because, as was reported in the same paper, the rate constant k could vary in consecutive runs under the same experimental conditions, as reflected by the two parallel dashed lines in Fig. 11. Nevertheless, the slope remained the same for all runs, permitting the extraction of a value of the activation energy E_a which could be attributed to the specific process under consideration.

At temperatures below 1770 K, a value for E_a equal to 195 kJ/mol was obtained, in close agreement with the value of 203 kJ/mol reported by L'vov, Bayunov and Ryabchuk [53] for the temperature range of 1380-1600 K. L'vov and co-authors attributed this value of activation energy to the competitive diffusion/vaporization process in a porous graphite medium ($E_a = 1/2(Q + \Delta H)$ - see the theoretical section). A value of the activation energy, also close to ours and equal to 184 kJ/mol at $T > 1400$ K, has been obtained by Sturgeon, Chakrabarti and Langford [52]. This value was related to the dissociation energy of the gaseous copper dimer. Some other data, reported in the literature, are as follows: Fuller [47] obtained $E_a = 138$ kJ/mol ($T > 1720$ K) and attributed this energy to the heat involved in the reaction of the reduction of copper oxide by carbon; Katskov and Orlov [57] presented an Arrhenius plot, from which a value of 154 kJ/mol could be extracted for $T > 1400$ K.

For the region of lower temperatures (below 1400 K, dashed line in Fig. 11), which was not examined in the present experiment, almost all reported values for E_a were very close to the enthalpy of vaporization of copper: $\Delta H_{1400} = 317$ kJ/mol [48, 52-53].

At high temperatures (above 1770 K), $E_a=77$ kJ/mol was obtained which closely coincides with the activation energy of 78 kJ/mol for the diffusion process reported in [54]. Another value for the activation energy, which was somewhat close to our result, has been obtained by Smets [48]: 50 kJ/mol at $T>1800$ K. The value obtained for E_a was attributed to the pure diffusion transport of the copper atomic vapor through the graphite partition, considering this transport not to be complicated by other concomitant processes (chemical reactions, sorption-desorption, etc.). Equations (22 and 23) were used to evaluate diffusion coefficients (D) in the temperature range of 1770-2600 K. Taking into account the geometry of the furnace, values for D between $3.7 \cdot 10^{-4}$ cm²/s and $2.0 \cdot 10^{-3}$ cm²/s were obtained over the temperature range studied. The frequency factor was determined from the intercept of the graph of $\log(k)=f(1/T)$ with the logk-axis at $1/T=0$ and was equal to $7 \cdot 10^{-2}$ cm²/s.

To verify the value of the diffusion coefficient obtained by using the tube furnace, another experiment was also carried out. A small graphite cup (height, 6 mm, inner and an outer diameters of 3.5 mm and 4.5 mm, respectively, and a depth of 4 mm) was used instead of the tube furnace. The cup was held between the same spring-loaded electrodes, as in the previous design, and could be tightly sealed by a graphite stopper. The stopper was made from the same type of graphite, as the tube furnace, and served as the filter to separate the analytical zone from a sampling volume. The thickness of the filter varied between 0.8 and 3.3 mm throughout the experiment. After the sample aliquot (10 μ L) containing 0.01 μ g of copper was introduced into the cup and dried, the cup was sealed by the stopper and heated by using a 3-step temperature program: charring (10 s, 900 K), atomization (up to 200 s, 1800 K), and cleaning (2 s, 2600 K). The intermediate steps (the initial atomization and the

short relaxation), used in the experiment with the tube, were excluded because the small thermal inertia of the cup allowed an instant vaporization of the sample. The absolute amount of the analyte was also reduced from 1 μg to 0.01 μg due to the much smaller volume of the cup compared to the tube. The analytical volume, from which the fluorescence was collected, was also reduced to $\sim 1 \text{ mm}^3$ in order to neglect a slight non-uniformity of the temperature over the filter surface and also to apply the model of steady-state diffusion through an infinite plane sheet. According to this model [56], the rate of transfer of the diffusing substance is the same across all sections of the filter and is given by

$$S = -D \frac{dn}{dx} = D \frac{n_1 - n_2}{l} \quad (24),$$

where D is the diffusion coefficient, l is the thickness of the filter, n is the number density of the analyte in the filter body, n_1 and n_2 are the number densities in the two surfaces of the filter. Under the boundary conditions of $n=n_0$ at $x=0$ (the filter bottom) and $n=0$ at $x=l$ (the filter top) and repeating the considerations (17-21) from the theoretical part, one obtains

$$k = \frac{D}{l^2} \quad \text{or} \quad D = kl^2 \quad (25),$$

where k is the rate constant for the diffusion process. The parameter k could also be obtained from the decay portion of the analytical signal by using an exponential fit.

The temporal behavior of the copper fluorescence signals, obtained at $T=1770$ K by using filters of different thickness (0.8 mm, 1.4 mm, and 2.5 mm), are represented in Figure 12. The rate constants, extracted from these signals, were 0.07 s^{-1} , 0.02 s^{-1} , and 0.009 s^{-1} , which result in values for the diffusion coefficients, via Eqn. 17 of $4.6\cdot 10^{-4}\text{ cm}^2/\text{s}$, $3.9\cdot 10^{-4}\text{ cm}^2/\text{s}$, and $5.8\cdot 10^{-4}\text{ cm}^2/\text{s}$, which gives an average $D=(4.7\pm 0.7)\cdot 10^{-4}\text{ cm}^2/\text{s}$.

The value for D , obtained at the same temperature (1770 K) for a furnace with a hollow cylinder geometry, was $3.7\cdot 10^{-4}\text{ cm}^2/\text{s}$, which is in a satisfactory agreement with this result.

Silver

Typical shapes of silver fluorescence signals for different atomization temperatures, together with temperature profiles, measured with photodiode using thermal radiation from the hot furnace, are displayed in Figure 13. One can see that as the temperature increases the kinetic of the release of silver atoms changes significantly: the long-tailed signal in Fig.13c transforms into the sharp, short spike in Fig. 13a. This likely corresponds to the transition from the dominant vaporization to the dominant diffusion kinetic as will be discussed below. A first-order exponential function gave a good fit (with a correlation coefficient close to 1) to the decay portions of the signals.

The Arrhenius plot for silver (Figure 14) was obtained over a temperature range of 1430-2280 K by using a five-step temperature program. Beyond this range, the uncertainty in measured rate constants exceeded $\pm 30\%$, and so these data were not considered to be

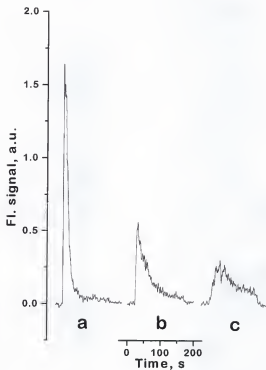


Figure 12. Fluorescence signal profiles for copper ($0.01\text{ }\mu\text{g}$) obtained at 1770 K by using a graphite cup atomizer sealed by the graphite stopper of the different thickness: a) 0.8 mm ; b) 1.4 mm ; c) 2.5 mm .

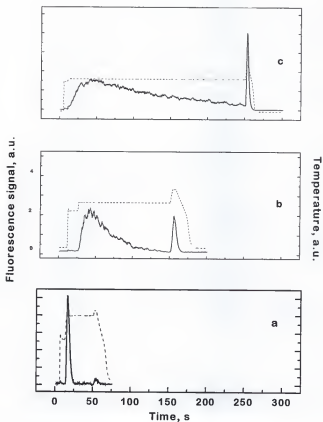


Figure 13. Fluorescence signal profiles obtained for silver ($1\text{ }\mu\text{g}$) at different temperatures: a) 2100 K; b) 1700 K; c) 1400 K. Temperature profiles vs time, obtained by using infra-red blackbody radiation from the furnace, are displayed by the dashed lines.

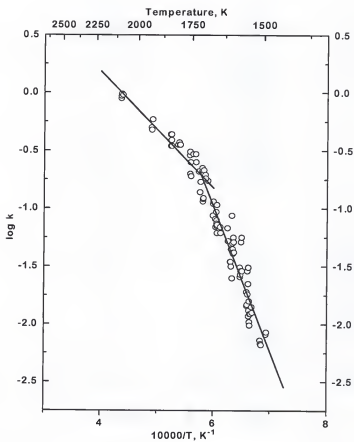


Figure 14. Arrhenius plot for silver.

reliable. It is seen that the plot consists of two linear parts. At temperatures below ~ 1750 K, the activation energy, corresponding to the atomization process, was equal to 238 kJ/mol. This value was in close agreement with that obtained by Katskov [51], 235 kJ/mol ($T < 1560$ K) and also closely coincided with the heat of vaporization of silver. Smets [48] obtained a value of 277 kJ/mol at $T < 1250$ K for vaporization of silver in a pyrolytically coated furnace. A value of the activation energy of 251 ± 12 kJ/mol, also close to ours, was reported by Katskov and Orlov [57] for a temperature range of 1100-1450 K.

Thus, one can conclude that after the first initial atomization and the relaxation steps (1900 K, 1 s and 1300 K, 5 s, respectively), the sample vapor has condensed on the inner surface of the furnace and then re-vaporized during the second atomization step. As was suggested by Fonseca et al. [58], vaporization of silver occurred preferentially from the surface of microdroplets. At relatively high masses (1 μg in our experiment) and moderate temperatures, the condensed phase could exist in the bulk of the graphite membrane during the total atomization time and be transported through it either by surface diffusion [53] or by simple capillary action [59]. It is interesting to note, that the inflection point in our plot corresponds to a higher temperature (1750 K) than the temperatures of inflection reported in other publications: 1560 K [51], 1450 K [57] and 1250 K [48]. This was probably due to the larger mass of the analyte (1 μg) which we used and the smaller inner volume of our furnace compared to those used by the above authors, favoring the condensation of the atomic vapor on the inner surface of the furnace in the form of microdroplets. For example,

Smets [48] used a mass of silver of only 0.2 ng and assumed that prior to the atomization, the sample was distributed as a surface monolayer. Under such conditions, the condensed phase could readily disappear at temperatures slightly above the melting point (1250 K, M.P. 1235 K).

At temperatures above 1750 K, a value of the activation energy of 97 kJ/mol has been obtained. A value of 103 kJ/mol was obtained by Katskov [51] by using a two-step diffusive graphite furnace with a pulse vaporizer at $T > 1560$ K. This value was attributed to diffusion, complicated by chemical interaction of silver with a graphite substrate. Fonseca and coauthors [58] used a furnace with a graphite platform to study the effect of the sample concentration, the pretreatment temperature and the roughness of the platform surface on the magnitude of the activation energy. Varying these parameters, they obtained values for E_a in the range of 97-147 kJ/mol and also concluded that the atomization process could slightly deviate from first-order kinetics. Nevertheless, when the thermal pretreatment was carried out at high temperatures (> 570 K), the process was shown to be first-order and the lowest value for E_a (97 kJ/mol), obtained in this case, was related to the desorption of silver atoms from the platform surface.

By comparing the Arrhenius plots for copper and for silver (Figs. 11,14) one can see that, contrary to copper, silver exhibits only one break in the Arrhenius plot. This can be explained by differences in the degree of interaction that copper and silver show for graphite. As was pointed out by Guell and Holcombe [60], copper possesses a strong affinity for the

graphite surface, whereas silver exhibits only a weak interaction with graphite [57]. Therefore, at moderate temperatures, when gaseous and condensed phases co-exist, we can expect that the process of atom release is driven by different mechanisms: by competitive diffusion/vaporization for copper and by vaporization from microdroplets for silver.

The values for diffusion coefficients within the temperature range of 1750 K-2280 K, estimated by using equations (14)-(15), were between $1.4 \cdot 10^{-3} \text{ cm}^2/\text{s}$ and $6.5 \cdot 10^{-3} \text{ cm}^2/\text{s}$. The preexponential factor D_0 was determined to be $1.1 \text{ cm}^2/\text{s}$. Compared to the diffusion coefficients which can be calculated on the basis of eqn. (23) by using the results from Katskov [51]: $E_a = 103 \text{ kJ/mol}$ and $D_0 = 29 \text{ cm}^2/\text{s}$, our values for D were approximately one order of magnitude lower. This was, probably, a result of differences in types of graphite used in these two experiments.

To verify the results obtained, a further experiment was carried out. Small graphite cylinders of length 1 cm and diameter 0.6 cm and density 1.65 g/cm^3 were used as diffusive media. The cylinders were tightly enclosed into an impermeable molybdenum tube of the same length. Two $20 \mu\text{L}$ -aliquots of the stock solution (1000 ppm of silver) were deposited on each end of each of the cylinders. After drying, the cylinders were placed into a temperature-stabilized laboratory furnace (Lindberg, USA) where they were annealed for 2 hours at a temperature of 900°C under an argon atmosphere. After this time, the graphite substrates were uniformly saturated by silver. This was checked separately for several cylindrical specimens by sawing off sections and determining the silver by LEAFS-ETA.

The solution of the diffusion equation for such a finite system is given by Jost[55] and can be well approximated by

$$\frac{n}{n_0} = \frac{8}{\pi^2} \exp[-t/\tau] \quad \tau = \frac{h^2}{\pi^2 D} \quad (26)$$

at initial and boundary conditions of $n=n_0$ for $0 < x < h$ at $t=0$ and $n=0$ for $x=0$ and $x=h$ at $t > 0$, where n_0 and n are the initial and current atomic number densities in the cylinder body, respectively, h is the cylinder length, D is the diffusion coefficient, and x is the coordinate along the direction of the diffusion transport. Consequently, τ and D may be obtained from the slope of the linear graph of $\log n/n_0$ vs time. The fluorescence signal profiles were measured at different temperatures in the same manner as in the previous experiments. The current values of n were determined by subtracting the portions of the analytical signal, integrated between $t=0$ and $t=t_1, t_2$, etc., from the total area of the signal. A similar study of the dynamics of the diffusant release is also described by Hensel and coauthors [61].

The plots of $\log n/n_0$ vs time, obtained at four different temperatures, are presented in Figure 15. The diffusion coefficients, calculated on the basis of the Eqn. (26), were $1.7 \cdot 10^{-3} \text{ cm}^2/\text{s}$, $2.1 \cdot 10^{-2} \text{ cm}^2/\text{s}$, $2.8 \cdot 10^{-2} \text{ cm}^2/\text{s}$, and $4.5 \cdot 10^{-2} \text{ cm}^2/\text{s}$ at temperatures of 1340 K, 1580 K, 1840 K, and 1970 K, respectively. The values for the activation energy and the preexponential factor, determined from the Arrhenius plot, were 109 kJ/mol and $17 \text{ cm}^2/\text{s}$. These parameters were very close to those obtained by Katskov [51]; $E_a=103 \text{ kJ/mol}$, $D_0=29 \text{ cm}^2/\text{s}$, and the diffusion coefficients listed above coincided with those given by Katskov within an uncertainty of $\pm 30 \%$. However, some discrepancy with our previous results

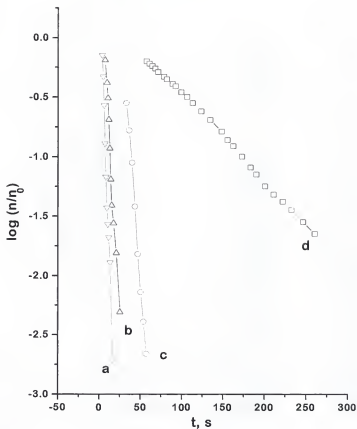


Figure 15. Diffusion out of the graphite cylinder bounded by the impermeable molybdenum surface, parallel to the axes of the diffusion transport, eqn. (26). a) 1970 K; b) 1840 K; c) 1580 K; d) 1340 K

($E_a=97$ kJ/mol, $D_0=1.1$ cm²/s) was observed. This was not very surprising because the two diffusive media in our two experiments were different in terms of surface-to-volume ratios: in the first case this ratio was equal to ~ 10 , and in the second, to ~ 2 . As has been shown [58-59], the surface topology can strongly affect the shape of the analytical signal and, consequently, the values of the activation energy and the diffusion coefficient. Also, Zherdev and Platonov [62] have pointed out that a combination of factors (the concentration used, the method's sensitivity, the time of diffusion annealing, etc.), involved in different experimental methods could distort the picture observed or emphasize only some of the features of the migration process. For example, analysis of the data on the diffusion of Cs in reactor graphite of various grades, scattered throughout the literature [62], showed that values of the diffusion coefficient could vary by as much as 8 orders of magnitude from author to author, although the scatter in values of the activation energy was relatively small.

Nickel

The activation energy for diffusion of Ni was found to be 161 kJ/mol over a temperature range of 1770 K-2530 K. No breaks in the Arrhenius plot were observed (Figure 16). A single-slope Arrhenius plot for Ni was also obtained by Katskov and Orlov [57] for temperatures between 1970 K and 2560 K with a value for the activation energy of 119 ± 8 kJ/mol. This value was attributed to vaporization of the metal from a microdroplet covered by a carbon core. According to the authors, the core can form on the microparticle of the melted metal if it possesses a strong affinity for carbon. The affinities for carbon were estimated (in %) for several elements and for the elements studied in the present work are: Ni - 2.6, Cu - 0.031 and Ag - 0.0018. As was shown, no core formed for Ag, some core

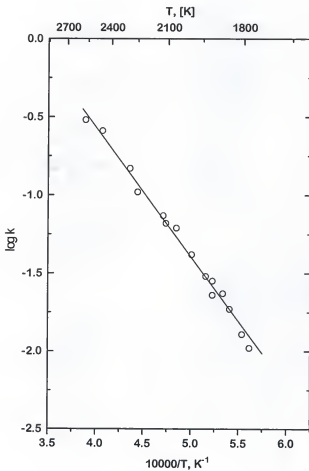


Figure 16. Arrhenius plot for nickel

formed for Cu but destroyed at relatively high temperatures, and a rigid carbonic core formed on the surface of molten nickel even at high temperatures.

Two values for the activation energy for Ni were reported by Sturgeon and coauthors [52]: 210 kJ/mol and 416 kJ/mol. The first one was related to dissociation of the gaseous nickel dimer whereas the second was associated with thermal vaporization of Ni from the condensed phase. The break in the Arrhenius plot occurred at a temperature of 1690 K (lower than the minimum temperature used in the present work).

An activation energy of 299 ± 17 kJ/mol ($2000 \text{ K} < T < 2440 \text{ K}$) was obtained by Rojas and Olivares [50], when a dry residue of a nickel standard solution was vaporized from the surface of a pyrolytic graphite furnace. First-order kinetics for the release of the metal vapor was proven.

The diffusion coefficients obtained on the basis of the model expressed by Eqns (17-23) were in the range of $5.6 \cdot 10^{-5} \text{ cm}^2/\text{s}$ - $1.5 \cdot 10^{-3} \text{ cm}^2/\text{s}$ ($1770 \text{ K} < T < 2530 \text{ K}$) with a value for the preexponential factor D_0 of $3.2 \text{ cm}^2/\text{s}$. The data for diffusion of Ni in electro-graphite, reported by Weisweiler and Nageshwar [54], were at least two orders of magnitude lower than ours. Such a large discrepancy with our results may be explained by a principal difference in the transport process in these two experiments. Diffusion of the metal into the bulk of a massive graphite prism [54] was carried out from a molten metal. Prior to the concentration analysis, the upper layer of the prism was removed, so that the influence of surface effects, which could take place, was minimized. In our case, when the surface-to-volume ratio was equal to ~ 10 , surface effects, such as sorption on surface irregularities or capillary action [58-59] could strongly affect the transport process. Also, the relative content of the two phases

(condensed and gaseous) on the surface of the porous diffusive medium is important because the transport mechanism, is supposed [62], to consist of a superposition of transport across the volume of the crystallites and vapor diffusion in the pore volume.

Conclusions

A method for the kinetic study of atomization and diffusion of three elements (Cu, Ag and Ni) in a porous graphite tube atomizer by means of laser excited atomic fluorescence spectrometry has been presented. Activation energies for vaporization/diffusion of Cu, Ag and Ni have been obtained for a temperature range of 1430 K - 2530 K and found to be in a satisfactory agreement with values of the activation energy reported by other authors. Diffusion coefficients for diffusion of the metal vapor through a porous graphite cylinder were estimated on the basis of the model proposed by Katskov [51] for a high temperature region. The values of activation energies and diffusion coefficients obtained in the experiment are given in Table 2 and Table 3, respectively.

The results of this study can be of importance both for further understanding of mechanisms involved in the formation and the transport of atoms in a porous graphite medium and for analytical applications. The difference in diffusion rates for different atomic vapors in graphite, obtained in the present work, together with the differential transport rates of molecular and atomic vapors, observed in previous studies [42], could be the basis for development of methods of high-temperature separation of constituents of complex matrices in order to improve the analytical performance of techniques utilizing ETAs (AAS, LEAFS, etc.), particularly, in terms of freedom from spectral interferences.

Table 2. Activation energies (in kJ/mol) of the release of atoms in ETAs: comparison of the data obtained in the present experiment with the literature

Temperature	This experiment	Literature
Copper		
< 1400 K	--"	317 [52-53]
1400 K - 1700 K	195	184 [52] , 203 [53]
> 1700 K	77	78 [54]
Silver		
< 1750 K	238	235 [51]
> 1750 K	97	103 [53]
Nickel		
1770 K - 2530 K	161	210 [52]

Table 3. Values for pre-exponential factor (D_0) and for diffusion coefficients (D)

Temperature	D_0 [cm^2/s]	D [cm^2/s]
Copper		
1770 K - 2600 K	$7 \cdot 10^{-2}$	$3.7 \cdot 10^{-4} - 2.0 \cdot 10^{-3}$
Silver		
1750 K - 2280 K	1.1	$1.4 \cdot 10^{-3} - 6.5 \cdot 10^{-3}$
Nickel		
1770 K - 2530 K	3.2	$5.6 \cdot 10^{-5} - 1.5 \cdot 10^{-3}$

CHAPTER 4

ANALYSIS OF COMPLEX MATRICES BY LEAFS-DIFFUSIVE TUBE ETA

Introduction

In the next experiment, the idea of the transport of the analyte vapor through a porous graphite filter was utilized together with a new arrangement of the LEAFS-ETA experiment. Contrary to the widely used practice of exciting atomic fluorescence within the hot graphite tube and collecting the analytical signal by means of a pierced mirror placed in front of the tube [8,24,36,63-64], in the present experiment, the fluorescence was excited directly above the outer furnace surface. This allowed for discrimination against the strong thermal background radiation produced by the furnace and for improvement of the fluorescence collection efficiency. The performance of the atomizer was studied in the course of the determination of silver in sea water. As was previously reported [40-41], the use of an atomizer with the graphite filter significantly reduced matrix effects; this is one reason why such a complex matrix as sea water was chosen for the real analysis. Silver was chosen because it exhibits excellent figures of merit for determination by LEAFS-ETA [33], possessing a high volatility and a low reactivity. Also, there are several studies in the literature concerning the determination of Ag in sea water [65-66]. The determination of Ag in solid standard reference materials (SRM) was

intended primarily for the investigation of the accuracy, feasibility, and versatility of the LEAFS technique with the diffusive tube atomizer.

Experiment

Solution samples of 10 μL were deposited into an inner graphite rod hollow (2, Fig.5) with an Eppendorf micropipet. When analyzing sea water, a 10 μL injection of sea water and a 10 μL injection of an aqueous standard were sequentially dispensed to the same spot of the rod hollow to obtain a calibration plot affected by the presence of the matrix.

A special sampler was designed to analyze solid powdered samples. It consisted of a narrow graphite cylinder with a stainless steel piston. One end of the cylinder was sharpened to a cone so that the cylinder tip was smaller than the size of the sampling hollow. The piston was lodged in a marked position and the sample powder was pressed into the channel. The powder was then released by pushing the piston down the cylinder channel. The average dosing mass (usually, in the range of 10-20 mg) of each sample was determined in advance in series of weighings. Weighing errors were taken into account in the calculation of concentration.

Two sets of silver standard solutions were used throughout the experiment. One set was prepared from solid silver nitrate (analytical-reagent grade, Fisher Scientific, Orlando, FL, USA) by dissolving 0.1575 g of the salt in 100 mL of high-purity water (18 M Ω cm) obtained from a deionizing water system (Milli-Q, Millipore Corp., Molsheim, France). Working standard solutions were then prepared by sequential dilution of this stock standard (1000 ppm of Ag) down to a concentration of 0.01 ppb. The second standard solution set

was obtained by a similar stepwise dilution of a 1000 ppm commercial Ag stock solution (Inorganic Ventures, Inc., Brick, NJ, USA).

Synthetic sea water was prepared from the solid salts of NaCl, Na₂SO₄, KCl, CaCl₂, and MgCl₂ of analytical-reagent grade (all from Fisher Scientific, Orlando, FL, USA) according to the recipe given in Khoo et al. [67] (Table 4). The certified reference materials (soils) SRM 2709-2711 (NIST, Washington, DC, USA) were used without preliminary preparation.

The dye laser output (656 nm) was frequency doubled by a KDP crystal to produce the 328 nm excitation wavelength. This was directed through a quartz window into an atomizer chamber (see Fig. 6) and was used to excite Ag atoms ($5s^2S_{1/2} - 5p^2P_{3/2}$ transition) generated above the diffusive tube furnace. The energy level diagram for silver, showing the transitions used in the experiment, is given in Figure 17.

Prior to initial use for analysis, new diffusive tubes were fired several times at 2500 °C until the signal, detected at the wavelength of silver transition (338 nm), dropped to the background level. The limiting background noise was primarily due to the laser radiation scattered from atomizer parts. It was significantly reduced by placing an acetone filter between the furnace and the monochromator slit and by blocking all possible sources of laser stray light. The width of the monochromator slit was 2000 μm, providing a high detector throughput and the best signal-to-noise ratio.

Before sampling, the furnace was fired several times at a temperature of ~2500 °C until the background signal fell to the baseline. Then the sample was deposited into the

Table 4. Major constituents of seawater [67]

NaCl	2.4 %
Na ₂ SO ₄	0.4 %
KCl	0.1 %
CaCl ₂	0.1 %
MgCl ₂	0.5 %

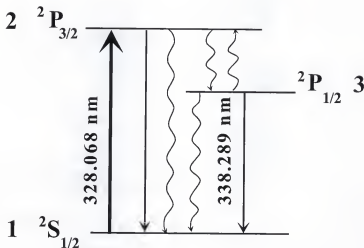


Figure 17. Simplified energy level diagram for silver. The laser excited transition is drawn with a thick solid line; fluorescence transitions with thin solid lines; and collisionally excited and deactivated transitions with wavy lines.

sampling hollow inside the furnace and 3-step heating program was applied. The program included a drying step (40 s, 110 °C), a charring step (10 s, 600 °C), and an atomization step (40s, 1500 °C, ramp rate 800 K/s). This program was used for all samples, unless otherwise specified. As the expected silver concentration in the sample increased, additional colored glass filters were placed between the furnace and the monochromator to avoid saturating the PMT.

Analytical calibration curves were obtained by using 10 μL aliquot of standard solutions which covered a concentration range of 6 orders of magnitude (0.1 $\mu\text{g/L}$ - 0.1 mg/L). The analysis of the sea water and soils was carried out within the calibration procedure to minimize a temporal drift of experimental conditions. The limit of detection (LOD) was estimated as the concentration of the analyte (silver) producing a signal 3 times the standard deviation of the blank (pure water).

Results

Spatial distribution

First, the 3-D distribution of silver atomic vapor diffused through the graphite tube was studied. Figure 18 (a,b) represents the distribution of silver atoms in X- and Y- directions (lengthwise and transverse with respect to the tube axis). The measurements were carried out under steady-state atomization conditions, i.e. at a steady state of atomic vapor flow. The steady state flow was established by placing a small piece of a pure silver wire into the furnace (continuous atomic source), and by holding the furnace at constant temperature (1500 °C) during the 4 min interval necessary to run one longitude or one transverse scan. The scan was done by moving the entire furnace relative to the exciting

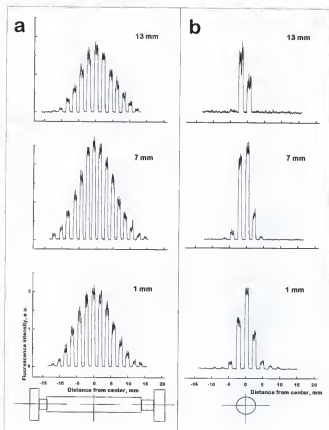


Figure 18. Spatial distribution of silver atoms diffused through the graphite tube with a stationary state of atomic vapor flow. (a) Silver fluorescence signals recorded at discrete distances (~ 2.5 mm) from the center of the furnace during one scan along the X-direction at different heights above the furnace; (b) fluorescence signals recorded in the same manner in the transverse direction (Y).

laser beam while leaving the collection optics fixed. The fluorescence was measured in a particular point for 5 s (with a volume of $0.25 \times 0.25 \times 2 \text{ mm}^3$) above the furnace, then the monochromator entrance slit was blocked for another 5 s while the furnace was moved to the next point, and so forth.

The distribution in the X- direction (Fig.18a) has a bell shape that probably reflects the atomic distribution within the furnace. For non-isothermal atomizers (like the one under study), the temperature inside the furnace reaches its maximum in the center and decreases towards the tube ends which contact with the water-cooled electrodes. This causes partial condensation of the atomic vapor near the tube ends and is responsible for the decrease of concentration in this part of the furnace. Diffusion of the vapor through the tube wall makes this effect even more pronounced because the diffusion coefficient is proportional to temperature.

The second observation is that the concentration of free silver atoms does not change significantly with the distance above the tube up to a height of 15 mm. This indicates, first, (not surprisingly), that under laminar argon flow (1 L/min) the transverse diffusion of the analyte vapor is much slower than the convection forced by the argon stream, and, second, that gas-phase reactions in the absence of matrix are insignificant even in a relatively cold zone far from the furnace. The latter confirms the conclusion given by Chekalin and Marunkov [64], who studied in detail the mechanism of silver atomization, that *"silver is one of the few elements for which chemical reactions, either gaseous-phase or heterogeneous, can be neglected under controlled conditions"* (p.1413). This statement, made in reference to a hot furnace enclosure, can now be extended to the environment near the furnace.

The distribution in the Y-direction (Fig.18b) is similar to the one along the X-axis and reflects the geometry of the tube.

The same distribution was also obtained for nonsteady state vapor flow conditions, when 10 μL of silver stock solution (1 ppm) was used as a sample. The similarity of the results for both steady state and nonsteady state flows indicates that the equilibrium distribution of free silver atoms is reached inside the tube prior to any significant diffusion of vapor through the furnace wall.

Also, relative rates of heating of different parts of the furnace were measured. To make this possible, a small orifice was drilled in the center of the tube and a telescope, terminated with a photodiode which detected infra-red blackbody radiation, was sequentially focused at the inner tube wall, the inner rod, and the outer wall through a set of diaphragms. Figure 19 shows the temperature vs time behavior for the three furnace regions. As can be seen, for the relatively low final temperatures (1100-1300 $^{\circ}\text{C}$, Fig.19a,b), heat dissipation predominates over heat supply due to the high thermal conductivity of graphite, responsible for the heat transfer from the hot central part of the tube to the water-cooled ends, and to the cooling of the furnace by the cold argon stream. In particular, the thermal conductivity mechanism affects the temperature of the radiationally heated inner rod which contacts directly with the water-cooled electrode. As the final temperature increases (up to 1500-1700 $^{\circ}\text{C}$, Fig.19c,d), this difference in heating rate becomes less; the inner and outer walls reach the final temperature almost simultaneously, while the inner rod lags slightly behind. All measurements were carried out at the atomizer control unit ramp rate specified as 800 K/s.

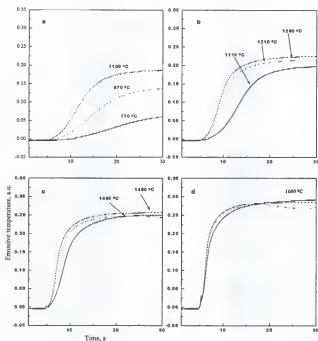


Figure 19. Temperature growth curves for different parts of the furnace: a,b - low temperature range; c,d - working temperature range. The dashed line corresponds to the temperature of the inner wall of the tube; dotted line to the outer wall; and the solid line to the inner graphite rod with a sampling boat.

This type of differential heating of the sampling zone and the bulk of the furnace is widely used in AAS carried out in furnaces with a platform [68-69]. These furnaces have been found to be advantageous with respect to simple graphite tubes without an insert, providing an enhanced analytical signal due to the substantial reduction in gas-phase reactions. This occurs because of the temperature delay between the platform and the bulk of the furnace allows the analyte vapor to enter the inner tube volume at a higher temperature. Our new furnace can, therefore, be considered as analogous to a furnace with a platform, prior to the diffusion of the analyte vapor through the porous graphite tube wall. Additionally, it is interesting to compare open tube atomizers with our sealed graphite furnace. Akman and Döner [70], who studied interference mechanisms of NaCl on Zn and Co using the AAS-ETV technique, showed that there are some losses of the analyte during the pretreatment (charring) step. This is due to formation (in the condensed phase) of volatile compounds which can be expelled from the open ends of the furnace before the atomization step. Also, according to Holcombe [71], thermal gas expansion and or matrix gas evolution are significant for analyte loss in open furnaces, especially, for volatile metals and high heating rates.

It is clear, that the closed graphite tube is free from these undesirable effects inherent to open tube furnaces. Even if a volatile compound of an analyte has been formed during the charring stage, this compound can be adsorbed on the furnace wall and then secondarily decomposed and evaporated at the atomization temperature. The presence of the graphite filter between the sampling and the analytical zones can also result in partitioning of the matrix gases and the analyte atomic vapor due to differing diffusion rates through the

graphite and to the formation of intercalated compounds implanted into the graphite crystalline structure [41-42]. This is the most likely reason for the reduction of matrix interferences in the atomizer with a graphite filter.

Saturation of the silver transition

The saturation parameter is an important figure of merit linked directly with other analytical characteristics, such as accuracy and limit of detection (LOD). Operating under saturation conditions is favorable because it provides the largest possible analytical signal, reduces flicker noise caused by fluctuations in the laser irradiance and interferences caused by variations in the quenching environment.

On the other hand, if the laser output far exceeds the optimum value, excessive laser scattering can significantly increase the background level and result in a poorer LOD. The latter is particularly important in our case, where stray laser light is a source of the limiting noise.

For these reasons, the saturation parameter was measured and compared with the theoretically estimated value. The fluorescence saturation curve (Figure 20) was obtained with the laser operating at its maximum power while recording the time integrated fluorescence signal, and gradually decreasing the laser irradiance by inserting into the beam before the atomizer chamber several calibrated colored glass filters to reach the region of linearity between the fluorescence signal and the laser power. The saturating medium (the silver atomic vapor) was considered to be optically thin when 10 μL of the 1 ppm concentration aqueous standard was atomized, and steady state fluorescence radiance

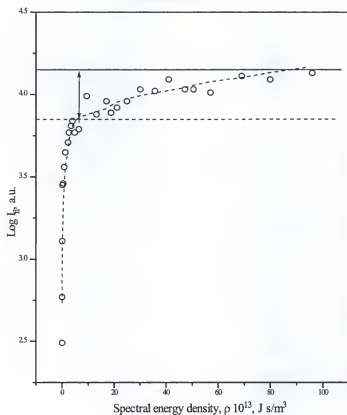


Figure 20. Saturation curve for $^2S_{1/2} - ^2P_{1/2}$ silver transition. The dashed horizontal line indicates 50% of the steady state saturation value.

conditions were assumed during the detection of the signal by the boxcar with a wide gate (50 ns) [72]. In accordance with the definition given in Omenetto et al. [73], the saturation parameter, E_{ss}^* , was determined as the laser irradiance producing a steady state value of the excited state population which is 50% of the steady state saturation value. In terms of energy, this parameter was found to be equal to 0.5 μJ .

The theoretical value of E^* , was estimated on the basis of the model proposed by Omenetto et al. [73]. Under our experimental conditions, silver can be considered as a sodium-like system (Fig. 17) in which the third level ($5p^2P_{3/2}$) is radiatively coupled with the ground state ($5s^2S_{1/2}$) and collisionally with the level directly reached by the laser radiation ($5p^2P_{3/2}$). It was evident from the experimental saturation plot that strong optical transitions 2-1 and 3-1 predominate over the collisional deactivation of levels 2 and 3; therefore, collisional deactivation has been neglected in the calculation. It was also assumed that rate constants responsible for the mixing of levels 2 and 3 ($\Delta E=921 \text{ cm}^{-1}$) are balanced, and the rate constant was derived from the experimental data obtained in reference [74]. As a result, the saturation spectral irradiance, E_{ss}^* , was calculated to be equal to $5 \cdot 10^{-9} \text{ J cm}^{-2} \text{ s}^{-1} \text{ Hz}^{-1}$ or, in terms of energy, 0.3 μJ , in excellent agreement with the experimental value.

In this way, the laser energy available in our experiment was found to be more than an order of magnitude in excess of the saturation spectral irradiance. This made possible to enlarge the laser cross-section (from 0.1 cm^2 to 0.25 cm^2) and, thus, to excite the fluorescence in a larger volume of the analyte vapor. In addition, calibrated colored glass

filters were used to further attenuate the laser irradiation to the point where it exactly satisfied the saturation condition.

Analysis of Sea Water

The determination of trace elements in sea water is pursued with great difficulty because, first, the high salt content of the sea water matrix often causes analytical inaccuracies and, second, the concentration of the element of interest is often below or very close to the detection limit of the most sensitive analytical techniques.

The most common methodologies used are atomic absorption spectrometry (AAS) [75-77], isotope dilution mass spectrometry (ID-MS) [65-66,78], and inductively coupled plasma mass spectrometry (ICP-MS) [79-80]. However, none of these methods is sensitive enough to detect ng/L concentrations without a preliminary separation/preconcentration procedure which can be very tedious in this matrix.

Recently, the use of the LEAFS technique with a graphite tube atomizer for the direct [25,81] and semi on-line [37] analysis of sea water and marine sediments has been reported. Cheam and coauthors [25] used the *in situ* standard addition procedure for the determination of lead in sea waters down to femtogram levels. No separation/concentration steps nor chemical modifier were used. Enger et al. [81] carried out the direct determination of antimony in environmental and biological samples at pg/mL concentrations. An intensified charge coupled device (ICCD) was used as a detector providing the possibility to control and correct for various background signals. Yuzefovski and colleagues [37] developed a method

for the determination of ultratrace amounts of cobalt in sea water by means of LEAFS-ETA coupled with semi on-line flow injection microcolumn preconcentration. Despite the adequate results obtained during the analysis of aqueous reference materials, the authors experienced contamination problems introduced by the preconcentration step.

In the present approach to the direct determination of silver in natural sea water, synthetic sea water was first used to develop a reliable calibration procedure. The normal aqueous standards calibration could not be directly used due to matrix interferences caused by the extremely high salinity of sea water which was responsible for an appreciable depression of the analytical signal, even in atomizers with a graphite filter [41]. Therefore, two calibration plots (Figure 21a) were created to account for the interferences. The first one was obtained by using aqueous standards, and the second, a 1:1 mixture of the synthetic sea water and the stock solution of a known concentration. The sample and the standard were sequentially pipetted into the sampling hollow of the furnace inner rod without premixing the individual solutions. Such premixing would seem more convenient to avoid the dosing sequence; however, the formation of a precipitate in the form of insoluble silver chloride, due to the substitution reaction of silver nitrate (the initial form of silver compound) with the excess of metallic chlorides contained in the sea water, leads to a highly inhomogeneous distribution of the precipitate in this hypothetical standard solution. The calibration plots shown in Fig.21a differ from each other by a factor of 0.23 (1.7 on a linear scale). This

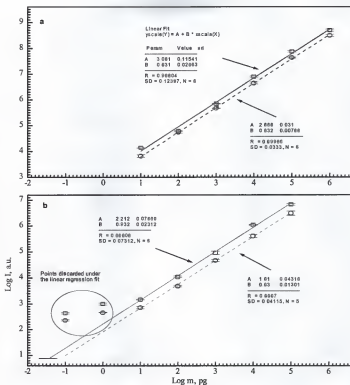


Figure 21. Calibration plots for the determination of silver in sea water. Solid lines represent the calibration on the basis of the stock aqueous solutions; dashed lines on the basis of 1:1 mixtures of the stock solutions with (a) synthetic sea water, and (b) natural sea water.

factor, which we denoted as a "depression factor", served to characterize numerically the matrix interference and served as a correlation coefficient allowing the determination of silver by using a normal aqueous standardization only. As can be seen, the two plots have exactly the same slope indicating complete recovery of the analyte.

A similar two-plot calibration procedure was then carefully repeated using natural ocean water samples. The samples were collected from the Atlantic Ocean near the central West coast of the Florida peninsula. Not surprisingly, in a series of consecutive experiments we found that the depression factor ranged from 0.28 to 0.32 (1.9 and 2.1 on a linear scale), reflecting an increased complexity of the real matrix with respect to the synthetic one. The log-log calibration plots (Fig.21b) were found to be linear in the range of 1 ng/mL - 10 µg/mL, corresponding to 10 pg - 0.1 µg. The slightly sub-linear slope of the graphs (0.93) can probably be attributed to a partial loss of the analytical signal at higher concentrations due to multiple reflections of fluorescent light from several colored glass filters which were used to keep the PMT within the linear dynamic range. The relative standard deviation (RSD) did not exceed 10% over the entire concentration range with a maximum of 9.5% at the 10 pg/mL level. A slight difference between the same calibration plots (solid lines in Fig.21a and Fig.21b) is due to the change in experimental conditions for consecutive runs which were carried out on different days. At concentrations lower than 1 ng/mL, contamination of deionized water by residual silver caused a curvature on the calibration plots; the data points corresponding to these concentrations were discarded under the linear

regression data fit. The blank was measured at the laser line detuned from the silver transition by 0.1 nm. This off-line signal was entirely determined by laser stray light when the pure water blank solution was atomized, and by non-selective molecular luminescence and laser scattering when a mixture of deionized water and sea water was used as the blank sample.

The fluorescence signal from the ocean water silver was 30-fold smaller than the last point made on either of the calibration plots and approximately 4 times higher than the threefold fluctuation of the background. Special care was taken to avoid procedural contaminations at such low concentrations. In the course of the experiment, it was found that laboratory air pollution affects the result of the analysis at concentrations below 1 ng/mL. This was due to the adsorption of silver from the air by the graphite tube surface, activated by multiple firings, during the several seconds after the atomizer chamber top was removed for consecutive sample dosing. The source of the air contamination was probably the open flame, located about 1.5 m from the furnace, in which a high concentration silver solution was occasionally used to set the laser wavelength. A typical signal from a low concentration aqueous standard is shown in Figure 22a. Peak 1 corresponds to the fluorescence of silver adsorbed on the furnace surface, and peak 2 to the fluorescence from the bulk of the sample atomized within the tube and diffused through it with some delay relative to the surface silver. This delay was caused not by only a spatial separation of the two sources of silver atoms but also by the differential heating rates of the outer and inner

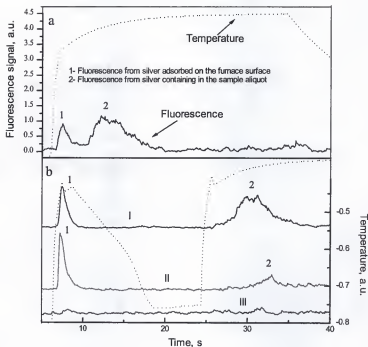


Figure 22. Signal profiles vs time. (a) No furnace preheating used: 10-fold attenuated signal from the aqueous stock solution (10 μL , 1 ppb); (b) Furnace preheating used: I - signal from the stock solution (10-fold attenuation, 10 μL , 1 ppb), II - signal from natural sea water (10 μL), III - off-line blank signal from sea water (10 μL). Dashed lines show the temperature of the furnace vs time.

furnace parts (see Fig. 19). The two signals could be easily time-resolved without changing the experimental conditions. However, the uncontrollable, sporadic character of the surface contamination very often resulted in overlapping of the two peaks, introducing an additional random error into the result of the analysis. Therefore, a special furnace temperature program was used over the whole concentration range to separate these peaks completely. The program included short and rapid (1 s, 800 K/s) heating to the atomization temperature after the drying and charring steps, short cooling (5 s), and then fast reheating and holding the furnace under atomization temperature during a time sufficient for the complete evaporation of the sample (20 s). Figure 22b shows the signal profiles obtained from the ocean water and the stock solution samples. The dashed line curve corresponds to the emissive temperature of the furnace measured by the photodiode. One can see that the two peaks are now completely separated and do not interfere with each other. The loss of the analyte due to the first, cleaning temperature spike was estimated not to exceed 5% which was within the instrumental error.

The degradation of the filter with increasing number of firings was controlled by periodic measurements of the fluorescence from an aqueous standard of 0.1 $\mu\text{g/mL}$ concentration. This signal remained stable over approximately 50 firings. This number of firings was taken as a life-time for one filter before it was replaced. A visual examination of the filter after multiple firings showed an increase in the roughness of the surface and

some defects in the points of electrical contact between the filter and the spring-loaded electrodes.

The influence of sea water sample volume on the magnitude of the analytical signal was also studied (Figure 23). As the sea water aliquot was increased, the signal showed a linear growth up to a volume of 30 μL . After that, a large quantity of steam, probably caused by the condensation of matrix constituents in the cold zone of the atomizer chamber, appeared in the analytical volume and masked the fluorescence signal. The chosen sample volume was 10 μL which provided no on-line preconcentration and a reduced blank signal relative to that when larger volumes were used. Additionally, using smaller volumes minimized plugging the graphite filter with excessive matrix material.

Finally, silver concentration in the coastal Atlantic seawater samples were determined by using the aqueous standards calibration plot. The analytical signal, averaged over ten measurements, was corrected for the off-line background signal and then multiplied by a factor of 2 (the depression factor) which introduced a correction for the matrix interferences. The concentration was found to be equal to 14 ± 6 pg/mL or, in terms of absolute values, 140 ± 60 fg. The results somewhat close to ours for the concentration of silver in different regions of the Pacific Ocean were obtained by ID-MS following preconcentration using a dithizone-chloroform extraction method (the concentration range of 0.5 - 3.2 pg/mL was reported to be uncertain) [65,82] and by AAS -ETA with a matrix modifier after solvent extraction and back extraction (5 - 8 pg/mL, RSD=10%) [66] (Table 5).

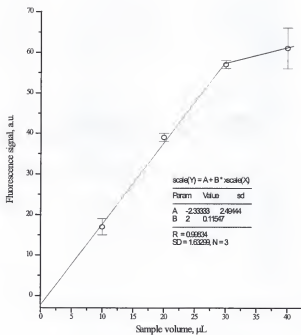


Figure 23. The magnitude of the silver fluorescence signal as a function of sea water sampling volume.

Table 5. Concentration of silver in seawater (pg/ml) obtained in this experiment in comparison with data from the literature

LEAFS - ETA direct analysis (coastal Atlantic)	ID - MS [65] preconcentration by extraction (open Pacific)	AAS - ETA [66] extraction, matrix modifier
14 ± 6	0.5 - 3.2	5 - 10

The LODs, obtained by linear extrapolation to $3\sigma_{\text{blank}}$ levels (blank signals were measured at the detuned from the silver transition line) were 40 fg (or 4 ppt relative) and 90 fg (or 9 ppt relative) when either pure aqueous or 1:1 mixed sea water standards (which were considered as real samples) were used for the construction of calibration plots, respectively. As seen from the literature, the absolute detection limit of 90 fg is among the lowest detection limits ever obtained for direct sea water analysis of silver.

Analysis of solid reference materials

Three moderately contaminated soil standards (SRM 2709 - SRM 2711; San Joaquin Soil, Montana Soil I and Montana Soil II, respectively) were chosen because they allowed an excellent opportunity to evaluate the behavior of this atomizer with direct solid sampling in the presence of a rather complex matrix.

The samples (soils) were highly homogeneous powdered substances with a high content of silicon (~30%) and organic matrix (~55%). After a calibrated mass of a particular SRM sample was placed into the sampling hollow, the furnace was heated by using the following temperature program: drying at 110 °C, 40 s; ashing at 800 °C, 25 s; and atomizing at 1500 °C, 30 s. During the atomization step, silver and silver compounds were released from the melted matrix, whereas the bulk of the matrix did not evaporate completely and left a glassy residue bead at the end of the atomization cycle. This bead was mechanically removed from the sampling hollow, and the furnace was cleaned at a higher temperature prior to the next sample dosing. An attempt to clean the furnace at very high

temperature (2500 °C), without removing the residue, failed. Although the rest of the matrix was evaporated, the performance of the graphite filter rapidly decreased, probably due to clogging of the graphite tube pores with matrix constituents. This degradation of the filter porosity could be deduced from observations of the gradual decrease in the fluorescence signals from aqueous samples which were injected after the cleaning cycles when the matrix residues were not removed.

Typical signal profiles obtained from the SRM and the stock solution samples are shown in Figure 24. It is seen that the two signals are delayed with respect to each other and the peak corresponding to the solid sample is much broader than that from the stock solution sample. The reason for such a delay and broadening is evident. In the case of the aqueous sample, after a drying step, the analyte is uniformly distributed as a very thin layer over the sampling hollow surface and can be evaporated almost instantly as the temperature of the surface reaches the required value. When atomizing a solid sample, the temperature of the bulk of the matrix raises at slower rate compared to a thin layer, and the release of the analyte from the entire volume of the melted sample droplet is a prolonged process governed by the diffusion of silver and silver compounds from within the droplet bulk to the droplet surface. It is worth mentioning in this connection, that the matrix frequently influences the rate of atomization and causes both the peak height and the peak shape to change, though the peak area is not affected and depends only on total number of atoms in the analytical zone during the atomization period [70].

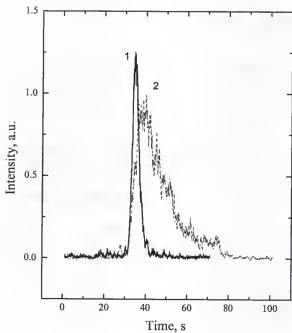


Figure 24. Temporal signal profiles: peak 1 - aqueous stock solution; peak 2 - solid reference material SRM 2709.

Table 6. Comparison of results (in $\mu\text{g g}^{-1}$) for the determination of silver in soil reference materials (data are $\pm 95\%$ confidence limits; $n=3$)

Reference material	Certified value	Determined value	RSD, %
SRM 2709	0.41 ± 0.03	0.35 ± 0.10	9.4
SRM 2710	35.3 ± 1.5	31.0 ± 3.7	5.7
SRM 2711	4.63 ± 0.39	4.75 ± 0.25	1.1

The results of the determination of silver in SRM samples are presented in Table 6. Based on Student's t-test at the 95% confidence level, there were no significant differences between the measured values and the certified values of the silver concentrations in the SRM's. The RSD's for the analysis of all SRM's were within 10%. The results indicated that both the precision and the accuracy of the method were satisfactory compared with the certified values.

Conclusions

The LEAFS-diffusive tube ETA method has been developed for the direct determination of femtogram levels of silver in sea water. Insignificant matrix interferences, causing only a 2-fold depression in the analytical signal obtained from the sea water sample relative to the one from the aqueous standard of the same silver concentration, were corrected by using a two-plot calibration procedure. No signal depression was observed when analyzing solid standard reference materials (soils). A good agreement of the results of the analysis with the certified SRM's values demonstrated the accuracy of the proposed method.

The sensitivity of the method can further be improved by the use of an isothermal furnace with a graphite filter instead of the non-isothermal one used in the present work. Also, the use of different types of graphite with different structure and porosity or other porous refractory materials for on-line partitioning of vapors of complex compositions can further minimize matrix interferences and improve the accuracy of the analysis when no adequate standards are available.

CHAPTER 5

LASER-INDUCED PLASMA AS AN ATOM RESERVOIR FOR LEAFS

Introduction

Plasmas, optically induced in the gas phase, were first described by Maker, Terhune, and Savage in 1963 [83]. Since then, the majority of studies have been spectroscopic in nature. Only in the past several years has laser induced breakdown spectroscopy (LIBS) (or laser ablation -LA) been used extensively as a practical method for the trace analysis of gas, liquid, and solid samples. Advancements in laser technology over the past three decades has made powerful lasers, needed for LA, more accessible, reliable, and easier to maintain. The recent popularity of LA as an analytical technique has generated a considerable number of publications [84-88]. However, the details of the breakdown process are still unclear and are still being investigated [89-91].

Breakdown occurs when a powerful laser is focused onto a solid surface. Power densities of the order of 10^9 W/cm² or greater are usually sufficient to cause breakdown in which high energy plasmas with high electron temperatures (10^4 - 10^5 K) and high electron densities (10^{15} - 10^{19} cm⁻³) are formed [92]. A phenomenological description of the plasma and post-plasma evolution is given in [87]; the sequence of processes involved is shown in Figure 25. When a short laser pulse strikes a surface, the surface temperature instantly increases past the vaporization temperature for any material. This occurs due to one- or

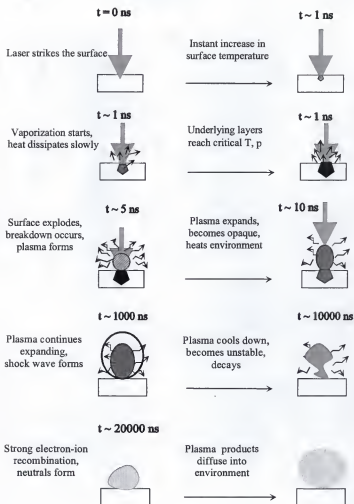


Figure 25. Evolution of laser plasma

multi-photon absorption, dielectric breakdown, and other (often undefined) mechanisms. The dissipation of energy through vaporization is slow relative to the laser pulse width. Therefore, before the surface layer can vaporize, underlying material reaches temperatures and pressures beyond the critical values, causing the surface to explode. The ablated material in the form of free electrons and highly ionized atoms expands at a velocity much faster than the speed of sound and forms a shock wave in the surrounding atmosphere. After several microseconds (up to tens of microseconds), the plasma plume slows down *via* collisions with ambient gas species, whereas the shock wave detaches from the plasma front and continues propagating at a speed approaching the speed of sound. At this stage, the plasma continues to decay through radiative, quenching, and electron-ion recombination processes that lead to the formation of high density neutral species in the post-plasma plume. The decay ends with the formation of clusters (dimers, trimers, etc.) *via* condensation and three-body collisions and with thermal and concentration diffusion of species into the ambient gas. This usually occurs within hundreds of microseconds (up to milliseconds) after the plasma has been ignited.

The plasma in the initial stage of its development is used in LA optical emission spectrometry (LA/OES), whereas the relatively cool plasma which follows can be additionally excited by a laser as in the LA-LEAFS [93] or LA/LEI [94] methods. In addition, the material which is removed by the LA plasma can be transported to other analytical instruments (ICP/OES, ICP-MS) [95] for subsequent detection.

There are several advantages of using LA for the analysis of solids. First, very little or no sample preparation is needed, greatly reducing the chance for contamination due to

handling and providing rapid analysis time. Secondly, due to the small amounts of ablated material (μg - ng), sample destruction is negligible. Third, the small area of the focused laser beam in LA gives rise to the possibility of microanalysis of solid surfaces with spatial resolution in the μm range. Fourth, LA allows the direct analysis of highly refractory materials because of the extremely high temperatures achieved in laser plasmas.

Nowadays, LA/OES is, probably, the most popular combination due to its simplicity and the possibility of simultaneous multielemental analysis. Sometimes, the plasma ablated by the laser is additionally re-excited by a high voltage spark or transported to a microwave or inductively coupled plasma. This usually results in better signal-to-noise ratios relative to the single step LA/OES method [95].

Likewise, the use of LEAFS in combination with LA can significantly improve analytical figures of merit in comparison with LA/OES [96].

LEAFS combined with laser ablation was first used for the measurement of radiative lifetimes of atoms by Measures and Kwong [97]. Lifetimes of three resonance transitions of chromium were determined with a high degree of accuracy using a Q-switched ruby laser as an ablation source and a nitrogen laser-pumped dye laser as the fluorescence excitation source. Shortly after this pioneering work, the same authors demonstrated the analytical utility of this technique. Chromium was determined at the ppm level in milk powder, flour, and steel samples [98]. It was concluded that the technique was relatively free from chemical interference effects under the experimental conditions used, and they suggested the possibility of a universal calibration curve for all elements irrespective of the solid matrix [98-99].

Since this early work, several tens of publications concerning the application of the LA-LEAFS combination for both spectroscopic and analytical purposes have appeared in the literature. Many of these applications appear in the reviews by Darke and Tyson [100] and by Radziemski [84]. In the field of spectroscopy, the LA-LEAFS technique has been used for diagnostics of laser generated plasmas [101-108] and for plasma imaging [109-110] in addition to the measurement of lifetimes [97,111].

The formation of gaseous metallic dimers using LA and laser induced molecular fluorescence was carefully investigated by Bondybey and co-workers [101-103]. Studies of such species provided insight into the metal-metal bonding and chemistry of metals. The species of interest (Pb_2 , Sn_2 , Cr_2 , and Be_2) were formed when the material which was ablated by a Nd:YAG laser was rapidly cooled by collisions with cold helium gas in a small chamber. The cooled vapor was then expanded through a small orifice into a vacuum chamber where molecular spectra were excited by a pulsed dye laser. Parameters such as internuclear distances and vibrational frequencies were derived from the spectra.

The spatial and temporal characteristics of laser induced plasmas on solid surfaces were studied by Piepmeyer and coworkers [104-106]. Both sample ablation and fluorescence excitation were carried out with microsecond flashlamp-pumped dye lasers. Their experimental design included a sampling chamber into which several different gases could be introduced. This arrangement allowed for studies on the influence of atmosphere on laser induced plasmas to be carried out. In addition to analyte elements, the spatial and temporal profiles of metal oxides were also studied [106].

Niemax and co-workers have also studied the temporal and spatial characteristics of laser induced plasmas [107]. In their work, a Nd:YAG laser operating at its fundamental wavelength was used for ablation and an excimer-pumped dye laser for fluorescence excitation. In contrast to the work of Piepmeier et al. in which only neutral species were measured, Niemax's group measured analyte ions in the plasma as well. Therefore, information about the ionization of analytes, including information about the spatial distribution of plasma temperatures could also be inferred. This group also reported on the use of LA-LEAFS for the study of collisional cross sections [108].

In addition to these spectroscopic studies, Niemax and co-workers have contributed several analytical papers involving the LA-LEAFS technique [29,112]. The measurement of silicon, chromium, and boron in steel samples resulted in detection limits of the order of a ppm, which is similar to those reported by Kwong and Measures [99]. However, Niemax reported a typical relative standard deviation of only 2-4%, which is significantly better than the values of 20-30% reported by Kwong and Measures. The excellent precision obtained allowed them to assess the homogeneity of several metallic matrices. More recent work included an investigation on internal standardization in LA-LEAFS measurements [29]. It was concluded that to a first approximation, elemental intensity ratios were independent of the matrix, amount of material ablated, and plasma temperature.

Evaluation of Limits of Detection

Limits of detection achievable by LA-LEAFS can be evaluated on the basis of the theory of the laser-solid interaction. The theory provides a computational tool for the evaluation of an absolute yield of atoms produced by laser ablation which then serves as

a departure point for the calculation of the minimum measurable signal obtained by the analytical measurement technique--LEAFS. However, such a theory does not exist and its construction is of little value, at least for analytical chemistry [104]. Indeed, any complete model of LA needs to consider too many parameters to be practical: besides those relating to the laser and those relating to the target, the pressure and the composition of the ambient atmosphere are of great importance. A large variety of potential sample materials (often with unknown properties) and experimental conditions make this problem practically insoluble.

Nevertheless, attempts have been made to develop practical theoretical models of the LA process. Two models of solid sample heating have been proposed by Bechtel [113]. The model of bulk heating implied that a laser beam was exponentially attenuated by the target with a small absorption coefficient. In contrast, the model of surface heating considered the situation when the absorption coefficient approached infinity providing that all laser energy was absorbed by the surface. The temperature and the temperature distribution was calculated for the interaction of laser light with the tungsten target: for moderate laser power densities (1 MW/cm^2) and for nanosecond pulse durations, the results were the same using both models, whereas for picosecond or shorter laser pulses, the bulk heating model gave a better prediction.

The amount of material vaporized by ordinary and Q-switched lasers was calculated by Ready [114] using conventional methods and a phenomenological model. Depths of holes produced by the lasers in steel, brass, aluminum, copper and nickel were in a satisfactory agreement with calculated values. Rosen and coworkers performed the experimental and theoretical studies of coupling of $0.35 \text{ }\mu\text{m}$ - laser radiation to aluminum

[115] and to titanium [116] alloys. The theoretical model included laser absorption in the target vapor through inverse bremsstrahlung and photoionization, and collisional energy transfer. The impulse coupling and plasma ignition threshold data were in good agreement with the data theoretically predicted. Harrach [117] used the heat-balance integral method to obtain an approximate analytical solution for the distribution of temperature on an opaque solid target which was exposed to intense laser radiation. Chan and Muzumder [118] have developed a model of the laser-material interaction accounting for the target damage by vaporization and liquid expulsion. The effect of laser power on the rates of removal, vaporization, and liquid expulsion was calculated for several metals (aluminum, superalloy, and titanium).

Walters and colleagues [119] have demonstrated that plasma ignition occurred on small ($0.1\text{ }\mu\text{m}$ - $0.3\text{ }\mu\text{m}$) and thermally insulated defects (flakes) of the target. They also proposed a simple theory of initiation of laser-supported detonation waves on aluminum. The results of this work have justified the approach by Arlinghaus and co-workers [120] using a thin (100 nm), isolated slice of the target (ZnS). Arlinghaus et al. [120] used this approach to calculate the surface temperature and to fit it (successfully) to the experimental data obtained at low laser fluence ($\leq 60\text{ mJ/cm}^2$). They have also studied the effect of the laser fluence (mJ/cm^2) on the absolute yield of Zn atoms. The numerical estimate of the number of atoms released was made by comparison of the optical emission signal from laser ablation with that from ion sputtering with known yield.

Hwang et al. [121] attempted to provide a simple mathematical relationship between mass ablated and laser irradiance which included the linear and the quadratic irradiance

terms. However, this theory seems to be invalid, because of incorrect combinations of equations from Rosen et al. [115].

Thus, although several theories have been proposed in the literature, it was very difficult to find a model which could be applicable to our experimental conditions which will be described in the next chapter and which could form the basis for a calculation of the mass ablated. Therefore, only a semi-empirical approach in which this mass is derived from the experiment can give a reliable estimate for detection limits. The average mass of a sample vaporized by one laser pulse can be calculated by weighing the sample before and after thousands laser shots and dividing the weight difference by the number of shots. The average masses removed from some metallic matrices (steel, brass, copper, zinc) by one laser shot were on the order of 20 ng (see next chapter).

As an example, let us estimate the relative detection limit of lead in copper under the conditions used in the experiment (see Chapter 6). 20 ng corresponds to approximately $N_{\text{Cu}} \cdot 2 \cdot 10^{13}$ atoms removed from the target. At the moment when the fluorescence of lead is excited at 283.3 nm and collected at 405.8 nm - 100 μs after plasma ignition, all of the ablated atoms are still confined in a compact region of space. This is seen from Figure 26 where a resonance shadowgraph of the LA plume is shown. The shadowgraph was obtained by igniting the plasma on the surface of pure lead and by illuminating the plasma plume by the expanded dye laser beam tuned in resonance with a strong lead transition (283.3 nm). The image of strongly absorbing plume was then formed on a fluorescent screen placed behind the plasma. Although the target was not copper, a rough estimate of the plume size at 100 μs delay time could be made. Taking into account the size of the analytical volume

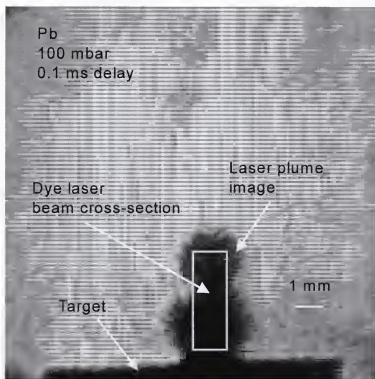


Figure 26. Resonance shadowgraph of the LA plasma generated on the surface of the pure lead target

projected into the monochromator and the size of the plume, the fraction of lead atoms, f , which contributed to the fluorescence signal, was estimated to be 0.3.

Because the fluorescence of Pb is saturated, the number of fluorescence photons N_p produced in the analytical zone by a laser pulse is given by

$$N_p = fN_{Pb} \left[1 - \exp\left(-\frac{g_3}{g_1 + g_3} A_{32} \tau_l\right) \right] \quad (27),$$

where N_{Pb} is the number of Pb atoms in the ground state, A_{32} ($0.89 \cdot 10^8 \text{ s}^{-1}$) is the Einstein coefficient of the transition at 405.8 nm, $g_1 = 1$ and $g_3 = 3$ are statistical weights of the ground state and the upper excited level [122], and τ_l (20 ns) is the duration of the laser pulse.

For the fluorescence collection system which includes the monochromator, the PMT, the current-voltage amplifier, and the gated integrator, the readout signal E (in V) averaged over n laser pulses is given by [123]

$$\overline{E} = \overline{N}_p \frac{\Omega}{4\pi} T \frac{GeR\eta}{\tau_g} \quad (28),$$

where Ω is the solid angle (0.1 sr), T is the monochromator throughput (0.26, dimensionless), G is the PMT gain ($5 \cdot 10^5$, dimensionless), e is the charge of an electron ($1.6 \cdot 10^{-19} \text{ C}$), R is the equivalent resistance of the PMT/amplifier circuit (500 VA^{-1}), η is the quantum efficiency of the PMT (0.15, dimensionless), and τ_g is the boxcar gate width (25 ns).

The ultimate limit of detection determined by only the shot noise from the optoelectronic circuit can be estimated on the basis of the equation [124]

$$\sigma_s = [2\Delta f(1+\alpha)eG\overline{RE}]^{\frac{1}{2}} \quad (29),$$

where σ_s is the root-mean-square (rms) of the background signal averaged over n laser pulses, $\Delta f = 0.886/n\tau_g$ (Hz) is the noise equivalent bandpass [124], and α is the secondary emission noise of the PMT (0.37, dimensionless). Taking into account Eqn. 28 and defining k to be equal to $(\Omega/4\pi)\eta T$, one can obtain the signal-shot-noise-limited expression:

$$\frac{\overline{E}}{\sigma_s} = \sqrt{\frac{k n \overline{N}_p}{1.772(1+\alpha)}} \quad (30),$$

which yields the detection limit expressed in the number of fluorescence photons equal to 35 (on the basis of the 3σ convention). This number of photons corresponds (via Eqn 27) to $N_{Pb}^{min} = 160$ atoms of lead which can be detected that yields the ultimate relative LOD as low as $N_{Pb}^{min}/N_{Cs} = 8 \cdot 10^{-12}$ or 8 ppt (parts per trillion).

However, the total instrumental noise includes not only shot noise but also other noise components (dark current noise, amplifier-readout (Johnson) noise, flicker noise, etc.). Typically, the noise rms (σ_{exp}) taken over $\sim 10^3$ laser shots is equal to ~ 4 mV. By making Eqn 28 equal to $3\sigma_{exp}$ and repeating the above considerations, the value for the minimum detectable number of atoms is found to be equal to $2.5 \cdot 10^4$, which yields a LOD of 10^{-8} (10 parts per billion--ppb).

CHAPTER 6

LASER ABLATION - LEAFS FOR REDUCED PRESSURE INERT ATMOSPHERE

Objectives

The small amount and spatial compactness of the ablated material are two factors which make LEAFS particularly appropriate for the analysis of the microplasmas generated by LA. This is due to the inherently high sensitivity of LEAFS and the small cross-section of the exciting laser beam (usually, several mm). Additionally, time-delayed atomic fluorescence can be excited from various intermediate energy states which remain highly populated for tens of microseconds (due to the high initial temperature of the laser plasma) and can possess higher excitation probabilities than transitions excited from the ground state.

Recently, Sdorra and colleagues [93] directly compared the LA-LEAFS technique with LA/OES by studying the same elements (silicon and chromium) in the same bulk matrix (NBS steel) under the same experimental conditions. The experiments were conducted under a controlled argon atmosphere (~100 Torr) using a Nd:YAG laser as an ablating source and an excimer laser pumped dye laser as an excitation source. Although the results for chromium yielded a lower LOD for the LEAFS measurements, (4 µg/g in LA-LEAFS vs 24 µg/g in LA/OES), a greater contrast between LEAFS and OES was seen in the course of the determination of Si. At a wavelength of 251.4 nm, the silicon emission yielded a LOD of only 200 µg/g with a linear dynamic range of 10^2 , whereas the fluorescence at 251.6 nm

used in LA-LEAFS resulted in a LOD of 600 ng/g with a linear dynamic range of 10^4 and percent relative standard deviations as low as 2 - 8%. The experiments were carried out under identical conditions and showed that the LIBS/LEAFS combination was more sensitive, although more complex, than LA-OES.

In the present work, the goal was to evaluate the analytical utility of the LA-LEAFS method for the determination of lead in various metallic matrices and for the lifetime measurement of the metastable level of lead. Four matrices with known concentrations of lead (see Table 7) were chosen for LA-LEAFS analysis. Lead was chosen because it was present in all samples and because it has a variety of strong atomic transitions suitable for laser induced fluorescence.

Experiment

A simplified block diagram of the experimental arrangement is shown in Figure 27. The ablating 308 nm-laser (Questek 2000 Series Excimer, Billerica, MA, USA), triggered by a pulse generator (Hewlett Packard 8003A, Boise, Idaho) at a frequency of 10 Hz, was directed through the quartz window into a small chamber containing a solid sample. The laser beam was focused onto the surface of the sample using a biconvex quartz lens ($FL = 70$ mm) to produce an irradiance of approximately 10^9 W/cm^2 on the surface. The cubic chamber (5 cm x 5 cm x 5 cm), which was made of stainless steel and had quartz windows on each face, was designed to be compatible both with vacuum and a controllable gas atmosphere. It was slowly moved (0.5 mm/min) as a whole in the horizontal direction providing a partially fresh spot on the surface of the sample for each consecutive ablating pulse. Approximately 2000 laser shots were delivered over 2 mm of the sample length.

Table 7. Standard reference materials used in the LA-LEAFS experiment at reduced pressure

Matrix	NIST SRM	Concentration (ppm)	*Melting Temperature (K)	*Vaporization Temperature (K)	Thermal Conductivity (Wm ⁻¹ K ⁻¹)
Copper (>99 % Cu)	496	0.41	1356	2840	401
	495	3.25			
	498	10			
	494	26.5			
	500	128			
Steel (>95 % Fe)	1265a	0.15	1808	3023	80.4
	1262a	4.3			
	1264a	240			
Zinc (>95 % Zn)	626	22	692.5	1180	116
	627	82			
Brass (~80 % Cu/ 20 % Zn)	1102	200	1183 - 1238		109 - 121
	1110	330			
	1109	750			

* Values as reported for pure elements (Cu, Fe, and Zn) by Goodfellow Corporation (Berwyn, PA, USA). For brass values are given for 70 % Cu / 30 % Zn alloy.

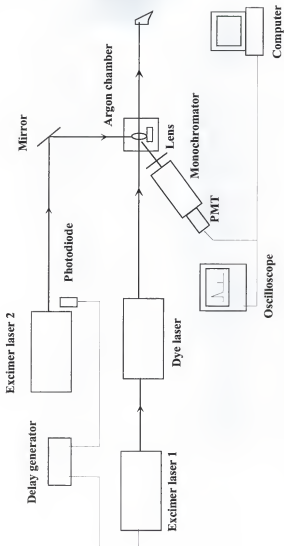


Figure 27. Simplified schematic of the experimental set-up

Scattered light from the ablating laser was used to trigger a delay generator built into the boxcar (model SR250) which was connected with a gate scanner (model SR200, both Stanford Research Systems Inc., Palo Alto, CA, USA). A gate with a fixed or scanned delay triggered a second 308 nm excimer laser (LPX100, Lambda Physik, Gottingen, Germany), which was used to pump one of the two dye lasers (EPD-330, Lumonics Inc., Ottawa, Canada). The dye laser output ($1.5 \text{ mm} \times 4 \text{ mm}$) was directed through the plasma plume at about 0.5 mm above the surface of the sample to excite fluorescence of Pb at 283.3 nm or at 357.3 nm (Figure 28).

The fluorescence emission at 405.8 nm or at 257.7 nm was collected at a right angle to the exciting beam. Two biconvex quartz lenses ($f = 60 \text{ mm}$, 45 mm diameter; $f = 100 \text{ mm}$, 50 mm diameter) imaged the plasma glow into a 0.24 m focal length monochromator with an effective aperture of $f/3.9$ and a grating blazed at 250 nm. The monochromator entrance and exit slits were 1000 μm , providing a high throughput.

The detection system for further signal processing included a PMT (model R928, Hamamatsu, Toyooka Vill, Japan), a 300 MHz voltage amplifier (model SR440) with a gain of ten, and a boxcar integrator (model SR250, both Stanford Research Systems Inc., Palo Alto, CA, USA) with a gate width of 25 ns. To keep the PMT in the linear range, the fluorescence signal was attenuated by a set of colored glass filters which were calibrated at the excitation and fluorescence wavelengths. The fluorescence signal was continuously monitored by a 500 MHz bandwidth oscilloscope (TDS 620A, Tektronix, Pittsfield, MA, USA).

The fluorescence signal from Pb in the laser plasma was averaged over 10 laser shots by using the boxcar averaging circuit. The sum of averaged signals over the observation time (200 s) was taken as an analytical signal. The detection limit was calculated based on the standard 3σ convention. Background measurements were carried out by detuning the laser wavelength by 0.1 nm from the center of the Pb line and repeating the same data processing as for the on-line measurements.

Analysis of the metallic matrices was carried out at reduced pressure under continuous flow of argon through the chamber with samples. The speed of the argon flow and the pumping rate were regulated by two precise needle valves to provide the constant pressure during the experiment. The samples were small plane sheets ($\sim 5 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$) of copper, brass, steel, and zinc sawed off from the standard SRM chips and rods. One plane of all sheets was mirror polished with polishing paper and then carefully rinsed with methanol. The samples were placed close to each other on the small plate inside the chamber and then were analyzed sequentially in the order of increasing concentration of lead, in one series to avoid a drift in experimental conditions. The fluorescence of lead was excited at 283.3 nm and collected at 405.8 nm at fixed delay and pressure providing the maximum signal-to-noise ratio.

In the lifetime measurement experiment, the pellet of pure lead was prepared from the lead powder (Fisher Scientific, Orlando, FL, USA) using a hydraulic press. In the first run, the fluorescence at 357.3 nm/257.7 nm of the excitation/collection wavelengths (exciting by the TMQ dye laser) was used to monitor the population of the metastable $6p_2^1D$ level,

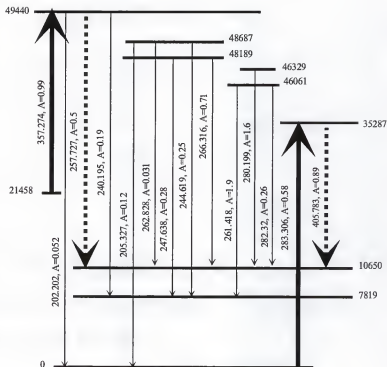


Figure 28. Simplified energy level diagram for lead. The laser excited transitions are drawn with thick solid lines; fluorescence transitions used in the experiment with thick dashed lines; other radiative transitions with thin solid lines.

whereas in the second run, the fluorescence at 283.3 nm/405.8 nm (exciting by the Coumarin 153 frequency doubled dye laser) was used to account for diffusional removal of atoms from the analytical zone. The delay time between the ablation and the excitation laser pulses was scanned between 500 μ s and 1 ms at a speed of 2.5 μ s/s in both runs. Three scans for each excitation/collection wavelength were carried out at each particular pressure.

Determination of Lead in Copper, Brass, Steel, and Zinc

For optimization of the experimental procedure, the copper sample (# 500) containing lead at relatively high concentration (128 ppm) was used. Two parameters were the subject to optimization: the delay time between the ablating and the exciting lasers and the pressure of argon. The delay time of 100 μ s and pressure of 100 Torr were found to be optimal to achieve a maximum signal-to-noise ratio. Two operational modes: gas-stop and gas-flow (0.2 L/min) were also evaluated in terms of their influence on the magnitude of the fluorescence signal. The gas-stop mode resulted in a calibration plot with a slope greater than unity. This was probably caused by accumulation of neutral atoms of lead in the analytical zone between consecutive laser pulses, especially, when samples with high lead content were used. Therefore, the gas-flow mode was used throughout the rest of the experiment.

As mentioned in Chapter 5, the mass ablated per a laser shot was of the order of 20 ng. More exactly, it was equal to 16 ng, 24 ng, 26 ng, and 14 ng for the stainless steel, the copper, the brass, and the zinc targets, respectively. Certainly, such small masses of the samples removed for the analysis can not be considered as representative to provide an

accurate determination of bulk concentrations. Even standard materials may exhibit considerable inhomogeneity on the scale sampled by a focused laser beam. Figure 29 shows fluctuations in fluorescence signals obtained over 200 s of continuous ablation (or ~2 mm in length along the surface) from different matrices. It is seen from Fig.29 that the distribution of lead in copper and in brass is relatively uniform over the large concentration range, whereas the distribution of lead in steel and zinc is not homogeneous causing large spikes in the intensity of the fluorescence signal. It is clear that by using short integration times (seconds) and several tens of laser shots, only a very small portion of the sample can be analyzed. Therefore, one can obtain a good accuracy of the results (several percent RSD) if this portion does not contain anomalies in the average distribution of the analyte to be detected. However, the high accuracy in this case will be reached at the expense of the precision and will provide a value for the local concentration which is not necessarily equal to the bulk concentration. Therefore, to improve the precision of the bulk analysis, long integration time (200 s) was used in order to relate average fluorescence intensities to the certified bulk concentrations of the standard reference materials.

To provide more details about the interaction of 308 nm-light with a particular material, scanning electron microscope images of grooves produced by the excimer laser on target surfaces were obtained (Figure 30). One can see from Figure 30 that the character of the interaction is very specific for each material: mild for copper and brass and vigorous, explosive for steel and zinc, with a large amount of molten droplet residues scattered around the grooves. On the basis of the model of the laser-surface interaction (see Chap.5, Introduction), it is clear that the lower the vaporization temperature and the higher the

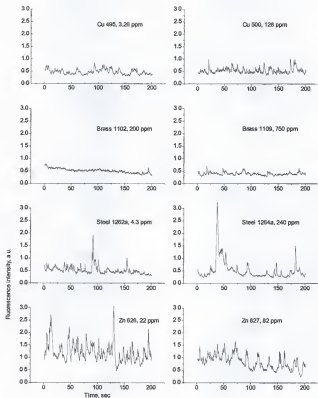


Figure 29. Fluctuations in fluorescence signals obtained from different metallic samples with different lead concentrations.

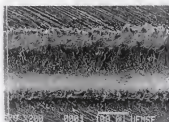
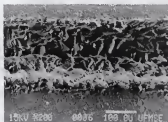
**A) Copper****B) Brass****C) Steel****D) Zinc**

Figure 30. Scanning electron microscope images of grooves produced by the excimer laser on surfaces of copper, brass, steel, and zinc.

thermal conductivity of the material, the more explosive is the process, the deeper the crater, and the more liquid-droplet phase is formed. This is seen from Fig.30d for the case of zinc which has lower melting temperature relative to the other matrices and a moderate thermal conductivity (see Table 7). A large number of spherical beads are scattered around the groove on the zinc sample. The size of the beads is up to 10 μm (Figure 31). Likely, the beads are formed due to explosive ejection of liquid and gaseous species into the space outside the breakdown zone, where they condense and then fall back to the surface under gravity. This is evident now, that despite the deepest track left by the ablating laser on the zinc surface (compare a,b,c, and d in Fig.30), the loss of mass, measured by weighing the sample before and after ablation, was the smallest (14 ng for zinc vs 24 and 26 ng for copper and brass, respectively). Therefore, the weighing procedure is not adequate to determine the real mass removed from the light-solid interaction spot giving from 2- to 3-fold lower values. This was checked by the mechanical removal of the beads attached to the surface and by the repetitive weighing of the "clean" sample. Nevertheless, the mass values, reported previously, were retained for detection limit estimates considering that only the vaporized fraction of the sample contributes to the analytical signal.

One more feature, observed in all laser traces (Fig.30, a-d), is a kind of a regular structure in the direction along the groove. This structure is likely the result of a motion of the target in discrete steps caused by the motor gear mechanism. Each regular pattern has a size of about 15 μm and is exposed to approximately 40 laser shots. The depth and the

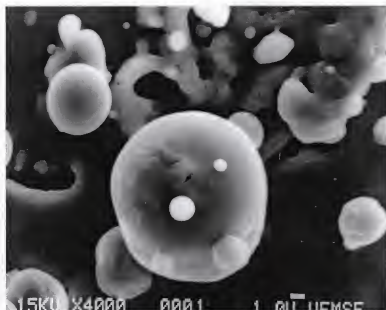


Figure 31. Scanning electron microscope image of beads produced on the surface of the zinc target as a result of explosive ablation

width of the grooves were estimated to be equal to 30 μm and 100 μm , respectively, providing the value for the spatial resolution of the method.

The calibration plot, constructed on the basis of standard samples used in the experiment, is presented in Figure 32. The plot is linear within the concentration range studied (0.15 ppm - 750 ppm), with log-log slope close to unity. Relative standard deviations (RSD) were within 20 % for all samples and were primarily the result of inhomogeneous distribution of lead within the samples.

In contrary to the results by Quentmeier et al. [29], who obtained separated calibration curves for Si, Cr, and Mn in three different matrices (steel, copper, and aluminum), the results of this experiment yielded the one calibration curve for the determination of Pb in copper, brass, steel, and zinc, though with the lower accuracy (20 % of RSD vs 2-5 % of RSD reported in reference [29]). This discrepancy in the results can be explained by the fact that the masses ablated by the Nd:YAG laser in [29] ranged between 30 ng (steel) and 130 ng (copper), whereas in the present experiment, the masses removed from the different matrices by the excimer laser were nearly the same. Secondly, the matrix dependent temperature of the plasmas in [29] resulted in different absolute populations of ground states of analyte atoms at short delay time (16 μs) used in the experiment, whereas in this work, the difference in plasmas temperatures could be considered as negligible at the moment of the fluorescence excitation (100 μs). Therefore,

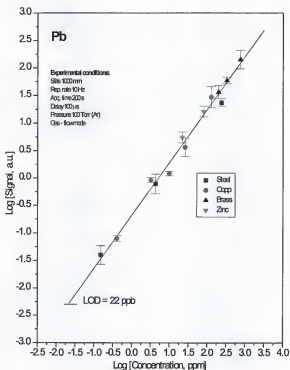


Figure 32. Calibration plot for the determination of lead in copper, brass, steel, and zinc samples.

no significant matrix effect was observed and there was no need for internal standardization as in [29].

A limit of detection of 22 ppb for the determination of lead in copper, brass, steel, and zinc SRMs was obtained based on the standard 3σ convention. Background measurements were carried out by detuning the laser wavelength by 0.1 nm from the center of the Pb line. This limit of detection is somewhat higher than was estimated in Chapter 5 (10 ppb). The difference in the obtained and the estimated values is most likely due to the stray light limiting noise in the experiment as compared to the shot noise limit used for the LOD estimation. The stray light was laser radiation scattered from components of the experimental set-up and from microscopic solid particles ejected into the analytical zone by ablation or formed there later as a result of condensation/recombination processes in the cooled plasma. Note that the LOD of 22 ppb corresponds to ~ 0.5 fg on an absolute basis which is among the best obtained by the LA-LEAFS combination.

Lifetime of the Metastable $6p_2^1D$ Level of Lead

Theoretical

As mentioned in Chapter 5, LA-LEAFS is a convenient tool for measuring lifetimes of atomic levels. Lifetimes of short-lived (ns range) atomic states can be determined by the excitation of fluorescence in the LA plume in a vacuum and observing the decay portion of the fluorescence signal (as in [97]). However, for metastable levels with lifetimes in the ms range, this approach does not work because atoms are removed from the analytical zone faster than any significant depopulation of the metastable level occurs. Therefore, to keep metastable atoms within the excitation zone longer, some sort of shielding atmosphere

should be used. Unfortunately, the presence of the atmosphere causes excited atoms to be deactivated not only radiatively but also collisionally. To account for this, the decay rate of the excited level is usually measured as a function of pressure with the consequent extrapolation of this dependence to zero pressure (see, for example, Alkemade et al. [125]).

In this experiment, the fluorescence was excited from the long-lived $6p_2^1D$ metastable level at 357.3 nm and collected at the anti-Stokes wavelength of 257.7 nm (Fig.28). Because of the short lifetime of the upper 49490 cm^{-1} level, the change in the magnitude of the fluorescence signal over a large time interval (hundreds of μs) should reflect the change in the population of the metastable level at 21458 cm^{-1} . We can, therefore, write

$$I_{257} \propto N_{ms} \exp\left[-t\left(\frac{1}{\tau_{ms}} + kp_{Ar}\right)\right] \quad (31),$$

where I_{257} is the intensity of fluorescence at 257.3 nm, N_{ms} and τ_{ms} are the population and the lifetime of the metastable level, and k [$\text{s}^{-1}\text{Torr}^{-1}$] is the rate constant of collisional deactivation of the upper level. To account for the "physical" removal of atoms from the analytical zone at times between 500 μs and 1 ms (the delay time interval used in the experiment), atoms were excited from the ground state at 283.3 nm and the fluorescence was collected at 405.8 nm. Considering the removal of atoms due to diffusion or gas phase reactions to be a first-order kinetic process, we obtain

$$I_{405} \propto N_0 \exp\left[-\frac{t}{\tau_r}\right] \quad (32),$$

where I_{405} is the fluorescence intensity at 405.8 nm, N_0 is the ground state population, and τ_i is the typical time constant of the decay process. First-order kinetics are often observed in the LEAFS-ETA (electrothermal atomization) technique. The LA processes at 0.5 ms time delay relative to the moment when the plasma was ignited can be considered as similar to the behavior of atoms in LEAFS-ETA, therefore, the first-order assumption is justified. Assuming further that the mechanism of the removal is the same for the atoms in the ground and in the metastable states, and combining (31) and (32), we obtain

$$I_{257} \propto N_{ms} \exp -t \left[\frac{1}{\tau_{ms}} + kp_{Ar} + \frac{1}{\tau_r} \right] \quad (33).$$

The $1/\tau_r$ term can be derived from the slope of the graph of $\ln I_{405}$ vs t , whereas the $1/\tau_{ms} + kp_{Ar} + 1/\tau_r$ term is obtained from the slope of $\ln I_{257}$ vs t . Then, plotting $1/\tau_{ms} + kp_{Ar}$ vs pressure (p), the value of τ_{ms} can be obtained from the intercept of this plot with the ordinate at $p=0$.

Results

Several processes, including collisional quenching, self-absorption, and reexcitation of atoms during the laser pulse, can distort the measurement of the lifetime of a metastable level by the fluorescence method proposed in this work (see the theoretical section). The collisional quenching effect is eliminated by measuring the decay rate of a metastable level as a function of pressure and by extrapolating this dependance to zero pressure. The difference in decay rates at different pressures is illustrated in Figure 33a, left column. One can see that the fluorescence at 257.7 nm from the 49440 cm^{-1} level (connected with the 21458 cm^{-1} metastable level *via* laser excitation) decays much faster at 0.5 Torr than at 0.1

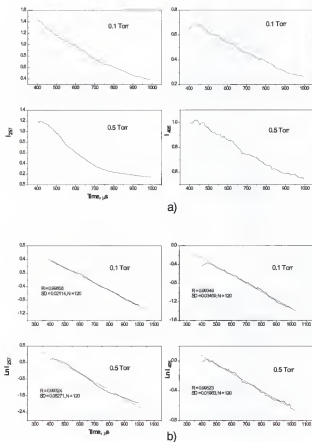


Figure 33. a) Intensities of fluorescence at 257.7 nm (left column) and at 405.8 nm (right column) vs delay time at different pressures. b) Same intensities in semi-logarithmic coordinates; the dashed lines show a linear fit to the functions.

Torr. Here, one should take into consideration that the change in the total number of atoms in the excitation zone, which is proportional to the fluorescence from the 35287 cm^{-1} level (measured at 405.8 nm and excited from the ground state at 283.3 nm), is a relatively slow function of time (Fig.33a, right column). The exponential character of both the decay of the metastable level and the dissipation of atoms from the analytical zone is confirmed by a good linear fit (with the correlation coefficient R close to unity) to the functions of $\ln I_{257}$ and $\ln I_{405}$ vs time, which are presented in Figure 33b.

Self-absorption of the fluorescence at 257.7 nm (and at 405.8 nm as well) is negligible at times between 0.5 ms and 1 ms after the ablation; the vapor of free atoms of lead in the analytical zone is optically thin due to fast expansion of plasma and post-plasma plumes in the low pressure argon atmosphere. This was indirectly confirmed by the resonance shadowgraph method (see Chapter 5): no significant absorption of resonant laser light at 283.3 nm was observed at delay times beyond $200\text{ }\mu\text{s}$.

Reexcitation, or cyclic interaction of atoms with a laser field, could, in principle, take place because the pulse length of the exciting laser (20 ns) was larger than the lifetime of the upper 49490 cm^{-1} excited state (5 ns) [126]. However, this effect was neglected considering that there are many other (besides the transition at 357.3 nm) strong radiative transitions from the 49440 cm^{-1} level (for example, at 240.2 nm - see Fig.28) and also from the levels collisionally mixed with the 49440 cm^{-1} level (48687 cm^{-1} , 48189 cm^{-1} , etc.). Therefore, the probability for the atom to get back to the metastable 21458 cm^{-1} level was not large.

Finally, introducing corrections for collisional depopulation and for the diffusional removal of atoms from the observation zone, the lifetime of the $6p_2^1D$ level was determined to be $50 \text{ ms} \pm 25 \text{ ms}$ (Figure 34). This result is a satisfactory agreement with the value of $37 \text{ ms} \pm 11 \text{ ms}$ [126]. The large error in the lifetime value obtained can be explained by the fact that the time scale used in this experiment (0.5 ms) was too short to provide a very accurate prediction of the lifetime whose value is almost two orders of magnitude larger. Nevertheless, the LA-LEAFS combination can be accepted as useful for measurements of not only short (in the ns range) radiative lifetimes as in the literature [97,111] but also for measurements of lifetimes of long-lived (in the μs or ms range) metastable levels.

Conclusions

It was demonstrated that the LA-LEAFS combination can be successfully used for the determination of lead in several metallic matrices (copper, brass, steel, and zinc) with a high spatial resolution ($\sim 50 \mu\text{m}$). The results of the analysis were free from matrix interferences under the experimental conditions chosen. The large integration time (200 s) provided an adequate determination of bulk concentrations, though with a moderate accuracy (20 % of RSD). The relative and absolute limits of detection of 22 ppb and 0.5 fg, respectively, are among the best reported in the literature for the LA-LEAFS method.

A potential of LA-LEAFS for spectroscopic studies was shown. The lifetime of the metastable level of lead was measured and was in good agreement with the value previously obtained by other techniques.

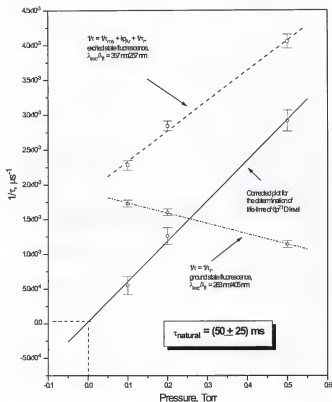


Figure 34. Plots used for the measurement of the lifetime of the $6p_2^1\text{D}$ level of lead. The dashed line is the rate vs pressure of depopulation of the metastable level due to natural and collisional decay and due to diffusional removal of atoms; the dotted line is the rate vs pressure of diffusional removal of atoms; the solid line is the rate vs pressure corrected for the diffusional removal.

CHAPTER 7 LASER ABLATION - EXCITED STATE LEAFS IN OPEN AIR

Objectives

It is evident that much work has yet to be done in the optimization of LA-LEAFS for the analysis of real matrices. For example, compact Nd:YAG and diode lasers can be used for the construction of a portable LA-LEAFS instrument for the routine application in a field. Such a compact spectrometer on the basis of LA/OES has recently been developed by Yamamoto et al. [127] for the analysis of metal contaminants on surfaces. The spectrometer included a compact Nd:YAG laser and a compact CCD-detector and was used for the direct determination of Ba, Be, Pb, and Sr in soils; Pb in paint; and Be and Pb in atmospheric particles. The detection limits (10 ppm - 300 ppm) were relatively high and could, probably, be improved by using the more promising LA-LEAFS combination. It is clear, that such a portable instrument should be operated in open air for reasons of apparatus simplicity

Also, the question still remains undecided, which of the two most frequently used lasers--UV or IR--is more favorable in terms of analytical characteristics. UV light can be more efficient than IR for the delivery of energy onto solid surfaces [84], resulting in more ablation per unit of pulse energy. The results by Geertsen, Sjöström et al. [91] also strongly suggest that UV laser sampling is better than IR with respect to reproducibility and reduced matrix interferences.

In the present experiment, the UV excimer laser ablation with the subsequent LEAFS technique were used for the direct determination of cobalt in three matrices: carbon, steel and soil in open air. The goal was to estimate the accuracy, feasibility, and versatility of the LA-LEAFS method by using it under unfavorable (open air) conditions.

Cobalt was chosen to be determined in soil, steel and graphite for the following reasons. First, cobalt plays a vital role in the nutrition of humans and other mammals [128]. This stimulates a search for new accurate and reliable methods for the determination of cobalt in environmental materials which take part in the nutrition chain. Second, cobalt is a common concomitant element which can effect the properties of iron matrices (steels). Therefore, the knowledge of bulk and surface concentrations of cobalt in steel is of significant importance for the improvement of technological processes and for quality control in steel production. In addition, cobalt is a convenient element to work with because it has a moderate reactivity (small chemical interferences in high temperature laser sparks) and a variety of strong atomic transitions suitable for laser induced fluorescence.

Experiment

The experimental arrangement was, in general features, the same as in the previous experiment (see Chapter 6, Fig. 27), excluding the chamber for a controllable gas atmosphere. The fluorescence of Co was excited either at 352.69 nm or at 352.98 nm. Tuning the dye laser to the wavelength of the cobalt atomic transition was carried out by exciting cobalt fluorescence in an air-acetylene flame in which cobalt stock solution was nebulized. A monochromator, a PMT, and a 500 MHz oscilloscope were used for signal

processing. The fluorescence signal from cobalt in the flame was visually monitored on the oscilloscope screen and maximized.

The delay between the ablating and the exciting lasers was 16 μ s. This delay provided the best signal-to-noise ratio, which was visually estimated by monitoring the fluorescence signal the oscilloscope.

The fluorescence signal (at 399.53 nm or at 402.09 nm) from cobalt in the laser plasma was averaged over 10 laser shots by using the boxcar averaging circuit. The sum of the averaged signals over the observation time (2 min) was taken as the analytical signal. The detection limit was calculated based on the standard 3σ convention. Background measurements were carried out by detuning the laser wavelength by 0.1 nm from the center of the Co line and repeating the same data processing as for the on-line measurements.

The Laser Ablation-ICP-MS experimental set-up, which was used to verify the results of LA-LEAFS analysis of soils, consisted of a Finnigan MAT SOLA ICP-MS and Finnigan System 266 laser accessory. Each soil pellet was exposed to approximately 400 ablating laser shots while translating the sample at a speed of 15 μ m/s. The mass spectrometer was operated in the peak jump mode with 5 channels measured for each isotope, a dwell time of 8 ms, and 128 passes per scan. A scan delay of 20 s was used in order to allow the signal to stabilize prior to measurement. In addition to ^{59}Co , the element of interest, ^{43}Ca or ^{44}Ca was also measured in order to account for variations in the ablated mass. This was necessary in order to provide an acceptable level of precision in the measurements (typically, 5-10 % RSD).

The method of standard additions was used for the determination of Co in soil and graphite. Several standards with known concentrations of Co were prepared by mixing the metal powder or the aqueous standard solution with finely ground samples. In the first case, cobalt powder (A6, Matheson Coleman and Bell, Norwood, CN, USA) was weighed and mixed with spectrochemical graphite powder (Graphite Grade UCP1, 200 mesh), to obtain a 10% (100,000 ppm) wt/wt concentration of cobalt in the bulk matrix. The mixture was rigorously shaken in a plastic vial containing plastic beads, for 1 hour. The set of lower concentration standards (down to 0.0001%, 1 ppm) was prepared by a sequential dilution of the first standard with graphite powder. Approximately 1.5 g of the powder mixtures were pressed into pellets (13 mm diameter, 2-3 mm height) using a hydraulic press and an evacuable die (Perkin Elmer Corp, Norwalk, CT, USA).

The second set of solid standards with the addition of stock solutions was prepared as follows. A 1000 µg/ml standard cobalt solution in 2% HNO₃ (Fisher Scientific, Fair Lawn, NJ, USA) was diluted with water to produce a set of solution standards with lower concentrations. Five ml of each solution standard was mixed with graphite powder (1 g) and placed in an oven for approximately 2 hours, at 110 °C until the wet paste was thoroughly dried. The graphite powder with residual Co from the solutions was then stirred again and pressed into pellets as described above.

The same procedure of the addition of solution standards was used with the powdered soil samples. The samples were soil standard reference materials SRM 2709 - 2711. One of them (SRM 2709) was certified for a cobalt content (13.4 ± 0.7 ppm). The

other two were not certified, with estimated concentrations of Co of approximately 10 ppm in each.

Determination of Cobalt in Soil, Steel, and Graphite

For the optimization of the experimental procedure pure cobalt samples pressed into pellets from a cobalt powder were used. Two different schemes of laser-excited atomic fluorescence were compared in order to maximize the signal-to-noise ratio. In the first scheme (see Fig. 35a), the laser fluorescence was excited from the ground state at 352.69 nm ($3d^7 4s^2 {}^4F_{9/2} - 3d^7 4s 4p {}^4F_{9/2}^o$ transition) and collected at a shifted wavelength of 402.09 nm ($3d^7 4p {}^4F_{9/2}^o - 3d^7 4s {}^4F_{9/2}$ transition). In the second scheme (Fig. 35b), the fluorescence was excited at 352.98 nm ($3d^8 4s {}^4F_{7/2} - 3d^8 4p {}^4G_{9/2}^o$ transition), from a level which has been thermally populated in the hot plasma, and collected at 399.53 nm ($3d^8 4p {}^4G_{9/2}^o - 3d^8 4s {}^2F_{7/2}$ transition). The excitation transition probabilities have only a 4-fold difference in the two schemes ($A = 0.12 \times 10^8 \text{ s}^{-1}$ vs $A = 0.48 \times 10^8 \text{ s}^{-1}$), whereas the fluorescence probabilities differed significantly ($A = 0.0092 \times 10^8 \text{ s}^{-1}$ vs $A = 0.36 \times 10^8 \text{ s}^{-1}$) [122]. Not surprisingly, the second set of transitions yielded a greater signal intensity, even when the fluorescence was excited several tens of microseconds after the plasma had been ignited. Figure 36 shows the evolution of the fluorescence intensity as a function of increasing delay time. One can see that the signal amplitude remains the same within a window of 5-15 μs and then decreases, approaching zero by 30 μs . A delay time of 16 μs corresponded to the maximum signal-to-noise ratio for the 352.98 nm / 399.53 nm scheme; this ratio was greater than that for the 352.69 nm / 402.09 nm scheme at any delay. The appropriate choice of the delay time

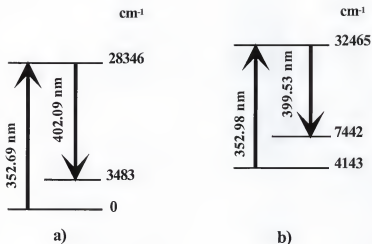


Figure 35. Simplified energy level diagram for cobalt. a) Fluorescence induced from the ground state; b) Fluorescence induced from the excited state

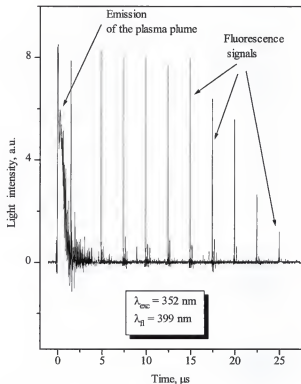


Figure 36. Intensity of the fluorescence vs delay time. Time equal to zero corresponds to the moment of a plasma ignition. The data was obtained by superposition of waveforms with different delays between the ablating and exciting lasers.

between the plasma ignition and the fluorescence excitation is crucial especially in the case of excited state fluorescence (as for the transition set of 352.98 nm/399.53 nm); the plasma should be hot enough to retain a high population in the excited state and cool enough not to contribute significantly to the background emission. This condition was checked for all matrices available in our experiments: pure cobalt, graphite, steel, and soil. Four combined emission/fluorescence spectra at 399.53 nm corresponding to four different matrices are presented in Fig.37. It is seen that the duration of plasma emission is different for different targets, ranging from several μ s for steel to approximately 10 μ s for graphite. After a delay of 15 μ s, the plasmas in all matrices had ceased to emit and therefore a delay of 16 μ s was found to be close to optimal for all four matrices.

As mentioned in the experimental section, two standard addition procedures have been used for the preparation of powdered samples (soils and graphite), namely, the addition of the metallic cobalt powder and the addition of the aqueous cobalt stock solution. Figure 38 shows the relative stability of the fluorescence signals obtained over 2 min of continuous ablation (or 2 mm in length along the surface) from different matrices (including those with powder and stock solution additions). It can be seen from Fig.38 that the addition of solid cobalt powder does not provide a homogeneous distribution of the analyte and gives an increase in fluctuations of the fluorescence intensity as the concentration of the powdered cobalt decreases. This occurs because of the small mass ablated (nanograms per laser shot) which is comparable with the mass of a single powder grain. In contrast, fluorescence signals from samples prepared using the stock solution addition procedure, show a very good stability approaching what was observed from the highly homogeneous stainless steel

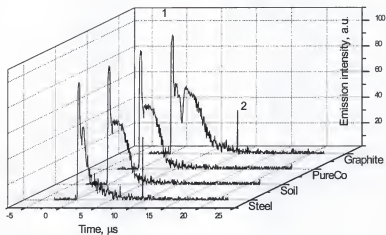


Figure 37. Emission of laser induced plasmas from different matrices. The initial spikes(1) are caused by the ablating laser pulse; the later spikes (2, shown only for steel and graphite samples) correspond to the delayed fluorescence of cobalt excited by the dye laser.

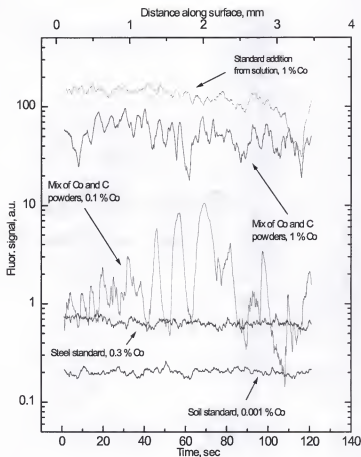


Figure 38. Fluctuations in fluorescence signals obtained from samples of different natures and different concentrations of cobalt.

samples. Therefore, in all the experiments, only samples prepared on the basis of the stock solution addition procedure were used for the analysis.

The average mass of a sample vaporized by one laser pulse was calculated by weighing the sample before and after about ten thousand laser ablation shots and dividing the total weight ablated by the number of shots. The average masses removed per laser shot were: 25 ± 10 ng for steel (NIST SRM 1265a), 150 ± 10 ng for pressed graphite, and 190 ± 10 ng for pressed soil (NIST SRM 2710).

The calibration plots constructed on the basis of the three different matrices (graphite, soil and steel) are presented in Figure 39. All three plots are linear within the concentration limits studied: 0.5 ppm - 5000 ppm for graphite, 25 ppm - 500 ppm for soil, and 70 ppm - 3000 ppm for steel, with log-log slopes close to unity. The absolute values of fluorescence signals obtained from matrices with the same concentrations of cobalt were approximately proportional to the masses ablated; the smallest signals were obtained from steel samples (25 ng ablated per laser shot), and the largest signals from soil samples (190 ng ablated per laser shot). Relative standard deviations were within 15-30 % for the low concentration range (0.5-100 ppm) and less than 10 % for larger concentrations (>100 ppm). A limit of detection of 0.2 ppm was obtained for the determination of Co in the graphite matrix, whereas the LODs for Co in soil and steel matrices were somewhat higher: 1 ppm and 20 ppm, respectively. The difference in LOD's becomes, however, less pronounced on an absolute basis taking into account the difference in masses ablated: 30 fg for Co in graphite, 190 fg for Co in soil, and 500 fg for Co in steel.

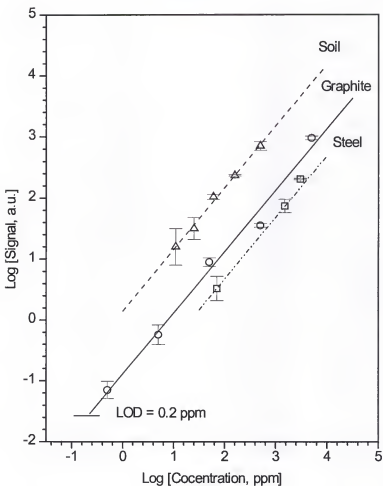


Figure 39. Calibration plots for the determination of cobalt in graphite, soil, and steel samples.

Approximately the same limit of detection (several ppm) for cobalt in soil was obtained by Ciucci et al. [129] using LA/OES with an IR laser for ablation in air. Slightly higher LOD's (10 - 300 ppm) were reported by Yamamoto et al. [127] when determining some other elements in soil (Pb, Sr, Ba, Be).

The limiting noise, when analyzing all three matrices, was stray laser light scattered within the plasma plume from microscopic solid particles. These particles are most likely either ejected into the analytical zone by the ablation process or possibly formed later as the result of recombination/condensation processes in the cooled plasma occurring 16 μ s after plasma ignition.

The results of the LA-LEAFS determination of cobalt in SRM samples (soils), using a multiple standard addition method, are presented in Table 8. Based on the Student's t-test at the 95 % confidence level, there was no significant difference between the measured value and the certified value of the cobalt concentration in the only certified standard reference material (soil SRM 2709).

A LA-ICP-MS technique, available in the laboratory, was also used to verify the results obtained by LA-LEAFS (see right column in Table 8). One can see that the divergence of the results obtained by the two techniques was insignificant, though the precision was somewhat better for LA-ICP-MS than for LA-LEAFS. The better precision was provided by the use of an internal standard (^{43}Ca or ^{44}Ca) in LA-ICP-MS. A LOD of 60 ppb was obtained for the determination of cobalt in soil, about 16-fold lower than in LA-LEAFS.

Table 8. Comparison of results (in ppm) for the determination of cobalt in soil reference materials (data are $\pm 95\%$ confidence limit; $n=3$)

Reference material	Certified	LA-LEAFS	LA-ICP-MS
SRM 2709	13.4 ± 0.7	12.8 ± 1.1	11.7 ± 1.6
SRM 2710	(10)*	9.9 ± 1.2	8.5 ± 0.8
SRM 2711	(10)*	7.9 ± 1.5	7.5 ± 0.4

As was shown in Chapter 6, detection limits at the ppb level can also be achieved in the laser ablation-laser induced fluorescence combination under somewhat more complicated experimental conditions. In addition to the present approach, where the ablation and the fluorescence excitation were carried out in open air, one can also use a reduced pressure atmosphere of a noble gas. A favorable collisional environment provides an enhancement in the atomic fluorescence and allows working at longer delays (up to 100 μ s - see Chapter 6) between the two laser pulses (ablating and exciting) thereby substantially reducing fluctuations in the background signal.

Conclusions

The excited state fluorescence of cobalt has been studied when analyzing graphite, soil and steel samples in open air. The fluorescence was excited from a level which was already populated in the ablation plasma and retained high population even at times when the plasma had almost ceased to emit. Such excited state fluorescence adds flexibility in choosing the most sensitive excitation/fluorescence atomic schemes including those which allow working at anti-Stokes transitions in a far-UV spectral range where continuous plasma emission is relatively weak.

In the present approach, the Stokes excited state fluorescence of cobalt was used, providing a better sensitivity in comparison with a traditional ground state excitation.

CHAPTER 8

TIME-RESOLVED RESONANCE SHADOW IMAGING OF LASER-PRODUCED LEAD AND TIN PLASMAS

Introduction

A promising way to study plasma and post-plasma processes, especially at times when the plasma has already ceased to emit, is visualization of the ablated plume by spectroscopic means. In one of the first works on LA imaging, by Basov et al. [130], the method of shadow photography was used. The plasma was induced on the surface of a graphite target by a 15 ns pulse from a Nd:YAG laser and was additionally illuminated by a Q-switched ruby laser producing a shadow plasma image on a photographic plate placed behind the target. The shadow was a result of deflection of the ruby laser beam in regions of high electron density gradients. A temporal resolution of 3 ns was achieved and the plasma behavior in a vacuum and at reduced air pressure was studied within the first 100 ns after the ablating pulse. In a vacuum, the plasma expansion velocity was estimated to be between $3 \cdot 10^6$ cm/s and $5 \cdot 10^5$ cm/s, whereas the speed of the visualized shock wave, propagating in the atmosphere of the vaporized material, was $\sim 10^7$ cm/s. Also, the electron density and the pressure within the plasma plume were measured and found to be $\sim 10^{17}$ cm⁻³ and $\sim 10^5$ atm, respectively. In a low pressure air atmosphere (2 Torr), the electron density and the shock wave speed, obtained on the basis of the interference method, were $4 \cdot 10^{18}$ cm⁻³

and $1.8 \cdot 10^7$ cm/s, respectively. The maximum plasma temperature behind the shock wave front with ~ 4 GW peak laser power was 100 eV ($\sim 10^6$ K). The conclusion was made that the method of shadow photography allowed the determination of the principle plasma parameters: the electron density distribution, the limiting velocity of plasma expansion, and the total mass.

Another shadow photography plasma imaging procedure with a similar experimental arrangement was recently reported by Kowalewicz and Eberl [131]. In this experiment, a pulsed CO_2 -laser (10^7 W/cm² in power density and 7 μ s in pulse width) was used for the ablation of metallic targets (Cu, Al, Fe) in air and a dye laser was used for a short (1 ns) plasma exposure. The plasma plume evolution within a 10 ns - 10 μ s time delay relative to the front edge of the ablating pulse was investigated and images of the expanding plasma plume along with images of the expanding shock wave were obtained. The shock wave velocity was estimated to be $4.9 \cdot 10^5$ cm/s (15 times the speed of sound) in the very beginning, $9.6 \cdot 10^4$ cm/s (3 times the speed of sound) after 5 μ s, and equal to the speed of sound after 10 μ s of plasma expansion.

Laser ablation imaging with the use of plasma emission collected into a two-dimensional gated CCD camera was performed by Castle and colleagues [132-133]. The temporal and spatial development for populations of selected levels of lead was studied within a spectral window of 357 nm - 374 nm. Time-resolved images of the emitting plasma were collected between 0.3 μ s and 4.3 μ s after the plasma was ignited by a Nd:YAG laser. A temperature on the order of 14000 K was estimated using a Boltzmann plot method. However, as was concluded by the authors, the temperature value obtained had to be treated

with suspicion because the plasma did not reach thermodynamic equilibrium within the time interval studied.

Laser ablation-laser induced fluorescence (LIF) with a CCD image detector was used by Sappey and co-workers [109,110,134] for the study of condensation and cluster formation processes in a post-plasma plume. The plasma was created by an excimer laser on the surface of a copper target and was illuminated by a dye laser beam focused into a thin sheet. The dye laser was tuned in resonance either with Cu or with Cu_2 fluorescence transitions. A two-dimensional map, reflecting the concentration of species in the plume at different times, was obtained. Quantitative analysis of the images was performed to estimate Cu and Cu_2 number densities and average velocities at different pressures of buffer gas (He or Ar) [109-110]. Kinetics of cluster formation was studied, and it was found that clusters (Cu_2) formed only after 100 μs - 200 μs relative to the point of plasma ignition, when the motion of the Cu vapor slowed to nearly a stop.

Thus, one can see that the imaging of laser ablation plumes over a large time scale is an extremely fruitful approach for measuring specific LA parameters and for understanding fundamental physical processes involved in light-surface interactions, as well.

The goal of the present work was to develop a new imaging technique for diagnostics of plasma and post-plasma LA plumes. The technique is based on the resonance absorption of laser light by the vaporized atomic cloud and on the consequent video recording of the plume shadow images which are produced on a fluorescent screen behind the target. Questions concerning plasma development and shock wave propagation will be discussed.

Experiment

The experimental set-up was, in general, the same as that described in Chap.6 and 7. Some new features of the experimental arrangement can be seen in Figure 40. The dye laser output, tuned in resonance with a strong atomic transition of the target material, was expanded by a beam expander to a size of approximately $1.5\text{ cm} \times 1\text{ cm}$ and was directed through the plasma plume so that no gap remained between the beam and the target surface.

The image of a strongly absorbing LA plume was then formed on a fluorescent screen (fluorescent paper) which was placed behind the target at a distance of 40 cm. The screen surface was tilted relative to the expanded laser beam at an angle of 45° (the angle between the surface normal and the beam). A TV camera (Model WV-CL354, Panasonic, Japan) was set above the screen at a distance of 1 m and screen images were recorded on a video tape. The camera was connected to a video monitor, providing an enhanced visual display of the space above the target during the experiment.

The target was a pellet of pure lead or pure tin prepared from lead or tin powder (Fisher Scientific) using an hydraulic press. The ablation was carried out in an argon atmosphere. The argon pressure, in the range of 50 mbar - 1000 mbar, was regulated by a precise needle valve and was constant during each run. The run consisted of approximately 2000 excimer laser ablating shots and the same number of dye laser imaging shots taken at different delay times relative to the ablation pulses. The delay time between the ablation and the imaging laser pulses was scanned between $1.5\text{ }\mu\text{s}$ and $200\text{ }\mu\text{s}$ at a speed of $1\text{ }\mu\text{s/s}$. Delay times below $1.5\text{ }\mu\text{s}$ could not be achieved in our experiment due to the large electronic jitter (tens of μs) of the ablating laser (Questek 2000) relative to the triggering pulse. The delay

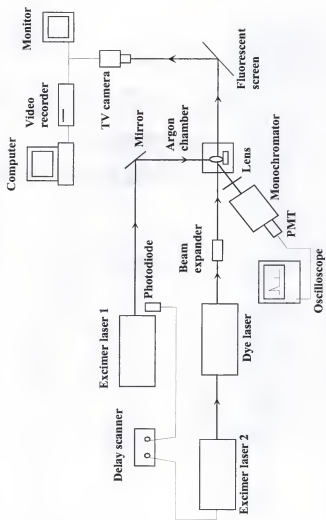


Figure 40. Schematic of the experimental set-up

time was also visually controlled by using a 500 MHz bandwidth oscilloscope which simultaneously displayed the initial plasma emission and the fluorescence signal from lead or tin excited by the same resonance imaging laser. The fluorescence was collected at a right angle to the imaging/exciting beam by using collecting optics, a monochromator, and a photomultiplier tube.

Shadow images of the lead and tin plasma and post-plasma plumes were obtained at frequency-doubled dye laser wavelengths of 283.3 nm and 286.3 nm, respectively. The fluorescence wavelength for the delay time monitoring was 405.8 nm for lead and 317.5 nm for tin. The images, recorded on a video tape, were selectively transferred into a computer format and then were manipulated by using CorelDRAW! (Version 4.0, Corel Corporation, USA) software. Corrections were made to account for geometrical distortion of the images due to the 45°-angle position of the screen relative to the imaging beam. To make this possible, horizontal and vertical scaling bars were placed on the target surface and their shadow images were recorded in the same manner as the plasma images but with the ablating laser blocked.

Analysis of Resonance Shadow Images

A series of resonance absorption shadow images of lead ablation plumes, obtained at different pressures and delay times, is shown in Figure 41. Each image is the result of one resonance dye laser shot taken at a particular delay time relative to the ablation pulse. One can see that in the early stage of plume development (first row in Fig.41), the images consisted of three distinct parts: a compact dark spot attached to the target surface which corresponds to the dense cloud of neutral atoms; a thin circle around the spot corresponding

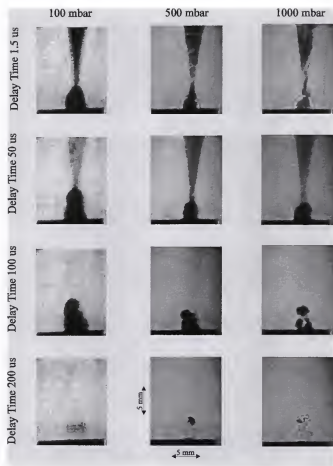


Figure 41. Evolution of the lead laser plasma and the absorbing cone at different pressures.

to the shock wave detached from the plume front and propagated in the argon medium; and a dark cone above the target which reflected the shape of the focused ablating beam. In contrast to the resonance atomic absorption images, the shock wave was visualized by deflection of laser light by the steep density gradient in a region of maximum compression of the medium (Ar).

The cone above the target appeared and stabilized after approximately 5 s or 50 laser ablation shots. It was likely formed due to photodecomposition of lead clusters or aerosol particles within the laser light cone.

As the delay time increased, the size of the LA plume became larger due to plume expansion (different at different pressures) and the cone became weaker (second row in Fig.41). After $\sim 75 \mu\text{s}$ the cone disappears and the plume becomes unstable (third row in Fig.41). After a delay of $200 \mu\text{s}$, almost no absorption of laser light can be observed for all pressures studied, although turbulence in the medium, visualized by deflection of laser light on the refraction index gradient, can still be seen near the target surface.

To elucidate the nature of the ablating cone above the target, two auxiliary experiments were performed. First, the presence of emission from the cone has been checked. The emission could be the result of a series of breakdowns produced in the divergent laser beam and occurring on small aerosol particles which were suspended in the argon atmosphere after condensation of the target material ejected by ~ 50 previous laser ablation shots. Such aerosol-induced laser breakdown was studied by Pinnick et al. [135-136] for liquid particles of $\sim 50 \mu\text{m}$ size. In our experiment, emission from the plasma plume was collected onto a 2-D CCD camera (ICCD-576S, Princeton Instruments, Trenton, NJ,

USA) in a direction perpendicular to the ablating beam. The wavelength-integrated image of the plasma plume is shown in Figure 42. One can see from Figure 42 that no other breakdowns above the target, other than the plasma itself, were detected. Therefore, the formation of the cone by absorbing free lead atoms was probably caused by UV decomposition of clusters. To confirm this, the ablating excimer laser beam was split into two mutually perpendicular beams so that the vertical beam was used for ablation and decomposition and the horizontal beam only for decomposition. As before, the space above the target was illuminated by the resonance imaging beam. Figure 43 shows a resonance shadow image obtained in this case. The cross-like shadow trace in Fig.43 corresponds to resonance absorption of dye laser light by free lead atoms produced by photodecomposition of clusters along the paths of both excimer laser beams.

The clusters could be diatomic lead formed *via* free atom condensation or three-body collisions in an inert atmosphere, as was observed for Cu_2 in a LA plume [109], and for Pb_2 and Cu_2 in a glow discharge [137-138]. However, an attempt to detect molecular fluorescence of diatomic lead at any of the wavelengths, mentioned in Patel et al. [137] (the 478 nm - 496 nm spectral range), was unsuccessful. Therefore, one can conclude that under the experimental conditions studied (a pressure range of 50 mbar - 1000 mbar and delay times of 1.5 μs - 200 μs), dimer formation is not efficient, whereas condensation of lead into larger particulates is more likely. Analysis of shadow images, obtained from lead and tin targets, showed that the condensation was efficient beyond $\sim 75 \mu\text{s}$ and $\sim 20 \mu\text{s}$ with respect to the ablation pulse for lead and tin, correspondingly, because no absorbing cones were observed beyond these delay times. Sappey and co-workers [109,134] have also reported

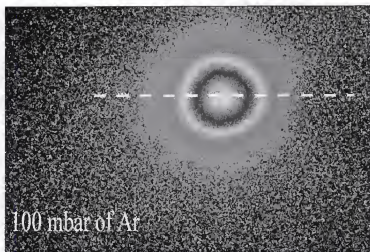


Figure 42. The wavelength-integrated image of the lead plasma plume obtained by using a CCD camera with $50\ \mu\text{s}$ gate delayed at $1.5\ \mu\text{s}$ with respect to the ablation pulse. The dashed line corresponds to the position of the target. The image above this line is due to the emission from the plasma; the image below is due to the reflection from the target surface.

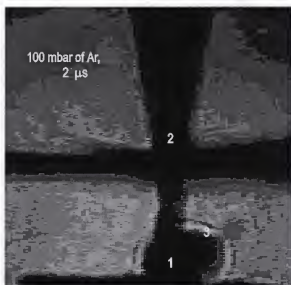


Figure 43. The shadow image produced by the split excimer laser beams. 1- resonance absorption within the plasma; 2- resonance absorption due to the cluster decomposition; 3- the shock wave.

that efficient condensation of copper in a LA plume had taken place in the late stages of plume development (hundreds of μs after plasma ignition).

The cluster photodecomposition in the excimer laser beam has likely occurred because of the large energy of the UV photon, compared to the bond energies of lead and tin. Indeed, the excimer laser photon at 308 nm has an energy of 4 eV, whereas the energies of Pb-Pb and Sn-Sn bonds are 86.6 kJ/mol and 187.1 kJ/mol [139], or 0.9 eV and 1.9 eV, respectively. Under the assumption of strong light-surface coupling, the clusters could therefore be easily dissociated due to light-induced cleavage of intermolecular bonds.

A series of shadow images, obtained from lead and tin targets at 100 mbar argon pressure and different delay times, is presented in Figure 44a. Analysis of the images showed a different character of light-surface interaction for the two targets. As can be seen from Fig.44a, the lead plume is uniform and grows toward the laser source, whereas the tin plume consists of two regions of different neutral atom density and has almost spherical symmetry. In addition, the tin absorbing plume along with the photodecomposition cone disappears much faster than that of lead; no resonance absorption can be detected after 50 μs for tin, whereas the shadow image of the lead plume can still be seen at delay times close to 200 μs (not shown in Fig.44).

The larger neutral atom density of the lead plume can be simplistically explained by the larger amount of material ablated from lead, compared to tin, due to the difference in physical properties of lead and tin. Lead has a lower vaporization temperature and a lower thermal conductivity than tin (2023 K and $0.353 \text{ Wcm}^{-1}\text{K}^{-1}$ vs 2876 K and $0.666 \text{ Wcm}^{-1}\text{K}^{-1}$) providing more vaporized material with less heat dissipation from the light-surface

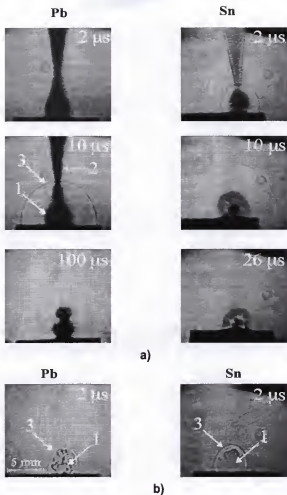


Figure 44. Shadow images of lead and tin laser plasmas at different delay times at 100 mbar argon pressure. a- laser is tuned in resonance with lead and tin atomic transitions; b- laser is detuned from the resonance by 0.1 nm.

interaction spot. Additionally, the amount of laser energy coupled to the lead surface is larger than to the tin surface due to the larger reflectivity of the latter.

One of the possible explanations for the difference in plume shapes and densities could be a memory effect reflecting the character of the light-surface interaction at an early stage (ns time scale) of the plasma development. Because of the high initial density of free electrons, the plasma can become opaque due to inverse bremsstrahlung at some instant during the laser ablation pulse (20 ns), blocking further penetration of laser light to the surface. This results in additional heating of the plasma which grows toward the laser beam [85]. However, the transparency of a plasma strongly depends on the target material. Fast expansion into the surrounding atmosphere along with strong optical emission may cool the plasma to the point where strong electron-ion recombination decreases the number of absorbing free electrons below the critical value and the plasma can again become transparent to laser light within the duration of the laser pulse. It is likely that this mechanism takes place for tin. As can be seen in Fig.44a (second row), by 10 μ s, the shock wave from the tin target has traveled a larger distance compared to that for lead, provided by the faster expansion of the tin plasma. As shown by Radziemski [85, p. 74], the plasma absorption coefficient is proportional to the square of the electron density and, therefore, to the square of pressure inside the plasma plume (under the assumption of complete ionization). So, one can suggest that the laser interacts with the tin surface almost continuously, as opposed to lead, and causes a continuous supply of the ablated material from one point on the surface. Logically, the distribution of matter in this case is almost

symmetrical with a larger particle density near the surface than in the periphery. To confirm this model, further experiments are necessary.

For comparison with the resonance shadow images, two non-resonance shadow images of lead and tin laser plasmas are also presented in Fig.44b. These images were obtained by detuning the laser from the lead or tin atomic transitions by 0.1 nm. One can see from Fig.44b that no features reflecting the presence of neutrals appear on the images, whereas the shock wave along with the plasma turbulence are distinctly visualized. Such non-resonance imaging can be more advantageous when studying early stages of the shock propagation (impossible in our experiment due to hardware limitations) because the shock wave image is not hidden under the strong resonance absorption shadow.

Shock Wave Propagation

The speed of the shock wave from the lead plasma was calculated by measuring distances between successive shock wave shadow images, taken at increasing delay times, and by dividing them by the corresponding time intervals. The time interval was determined by the complete separation of two images and was equal to 2 μ s. Hence, the speed measured was a mean velocity averaged over 2 μ s of the shock propagation.

Figure 45 represents the dependance of the shock wave speed vs the delay time at different pressures. As seen from Fig.45, within the first ~ 10 μ s of the shock propagation, shock wave velocities lie between 470 m/s and 710 m/s, depending on pressure, and approach the speed of sound by a delay time of ~ 20 μ s. The speed of sound in an ideal gas atmosphere (like argon) does not depend on pressure and can easily be calculated by using the classical equation

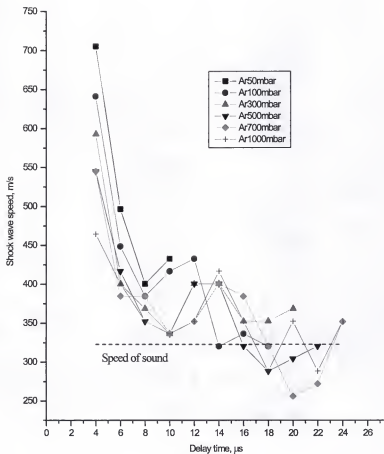


Figure 45. Speed of the shock wave vs the delay time at different pressures. The dashed line shows the speed of sound in argon.

$$c = \sqrt{\gamma \frac{RT}{M}} \quad (34),$$

where c (m s^{-1}) is the speed of sound; γ (dimensionless) is the adiabatic constant; R ($\text{J mol}^{-1} \text{K}^{-1}$) is the universal gas constant; T (K) is the temperature; and M (kg mol^{-1}) is the atomic weight. On the basis of Eqn (34), the speed of sound in argon was calculated to be equal to 323 ms^{-1} . The argon ideality was checked by the comparison of the specific heat capacity for an ideal gas $c_p = 5/2 R = 20.775 \text{ J mol}^{-1} \text{K}^{-1}$ (see, for example, [140]) with that tabulated in [139]: $c_p = 20.786 \text{ J mol}^{-1} \text{K}^{-1}$ at normal conditions.

Theoretically, the speed of a shock wave can be estimated from the equation proposed in [85] for a laser-supported detonation wave (LSD):

$$V_s = \left[\frac{2(\gamma^2 - 1)E_p}{\rho_0} \right]^{1/3} \quad (35),$$

where v_s (m/s) is the speed of the detonation wave, γ is the adiabatic constant of the medium, ρ_0 (kg/m^3) is the ambient gas density, and E_p (W/m^2) is the irradiance absorbed by the plasma. However, in practice, the value of E_p remains undefined since no rigid theory exists allowing the estimation of this parameter. Indeed, the only parameter known in the experiment is the total laser irradiance, E_0 , which is related to E_p by

$$E_0 = E_p + E_r + E_s \quad (36),$$

where E_t is the irradiance transferred to the target, and E_s is the irradiance lost to the environment. Despite numerous theoretical models for laser-surface interaction which have been proposed in the literature [113-120], none of them permits a practical calculation of E_p for an arbitrary system. Therefore, to compare the results of this experiment with those predicted by the theory for LSD (Eqn.35), it was assumed that only 10% of the incident laser light was absorbed by the plasma (there are some indications of the validity of this estimate in [85]) which supports the shock wave.

Figure 46 shows the experimental (a) and the theoretical (b) dependence of the shock wave velocity upon the argon density, based upon Eqn. 35. The experimental curve for v_s vs ρ_0 at a delay time of 5 μ s was obtained by a computer fit of the $v_s = a_1 \rho_0^b$ function to the experimental points, where a_1 and b are variable parameters. One can see from Fig.46 that the experimentally measured speed is ~50-fold lower than the theoretical estimate, showing the weaker dependence upon density ($v_s \propto \rho^{-1/6}$ in the experiment vs $v_s \propto \rho^{-1/3}$ in the theory). This discrepancy can easily be explained on the basis of the fact that the shock wave, observed in our experiment at the stage when it had already detached from the plasma front, was no longer a laser-supported detonation wave, for which Eqn.35 is valid, but rather a compression wave propagating on its own and retarded by the argon atmosphere. Nevertheless, it still retains some memory of what has happened to the plasma at earlier times during the ablating laser pulse. One can, therefore, conclude that the proposed method of shock wave imaging is appropriate for understanding the plasma behavior during its late stages, whereas the interferometric method proposed in [130] seems to be more relevant for

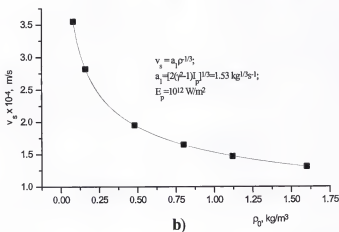
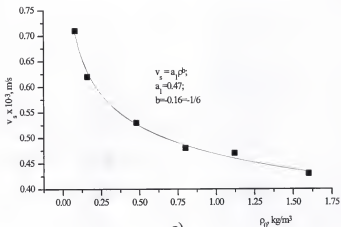


Figure 46. Speed of the shock wave vs ambient gas density. a- experimental data taken at the delay time of 5 μs ; b- theoretical curve obtained on the basis of Eqn.35.

the verification of the theory of laser-supported detonation in the beginning of plasma development.

Conclusions

The method of resonance shadow imaging of lead and tin laser-induced plasmas has been evaluated. Analysis of the images provided qualitative spatial information about the neutral species density within the plasma and post-plasma plumes at times between 2 μ s and 200 μ s and under different argon pressures (50 mbar - 1000 mbar). Also, information about cluster formation and shock wave propagation has been derived from the images.

This method can further be improved in terms of obtaining quantitative information by using a simple optical transducer (e.g., a photodiode array or CCD) in place of the fluorescent screen.

CHAPTER 9

CONCLUSIONS AND FUTURE WORK

In contrast to molecular separation methods which are based on structural peculiarities of molecules, separation of atoms is a more complex problem due to the less pronounced structural difference between elements. One of few possibilities to separate elemental components is to make them diffuse through dense media utilizing differential rates of the diffusional transport of elements. In addition, this transport has to be carried out at high temperatures to keep atoms dissociated.

The attempt made in this work to separate components of very complex matrices by means of diffusion through hot graphite can generally be accepted as successful. In comparison with conventional ETAs, the use of the diffusive tube furnace provided a significant reduction in matrix interferences and still resulted in a very high sensitivity for the LEAFS analysis. Further improvement of this technique should primarily be directed toward finding inert refractory media better than graphite and designing more adequate hardware. The latter includes experimental components which can provide fast and controllable regulation of the furnace temperature. The diffusive furnace itself should be re-designed to provide higher isothermality than in the present experiment, at least in the essential region where diffusion occurs.

Considering the fundamental aspect of high temperature separation, precise measurements of diffusion rates for elements in diffusive media (particularly, in graphite)

should be continued. The present work showed that LEAFS is a perfectly suitable technique for obtaining such fundamental information. It would also be a good idea to combine atomic and molecular fluorescence in order to obtain a detailed map of species present in the analytical zone after separation. Laser-induced fluorescence certainly has potential for such a study.

As was mentioned in Chap.5, many of mechanisms of laser material interaction are not fully understood and need to be further investigated by the largest possible variety of techniques. LEAFS is one of them, offering the unique possibility to measure fundamental atomic constants, atom transformation rates, and concentrations of species in laser plasmas. This work demonstrated that LEAFS can be successfully used for either analytical or spectroscopic purposes with minor or without changes in the experimental design.

The determination of lead in metallic matrices at the ppb concentration level by using a universal calibration curve for all samples can be considered as a certain breakthrough in the practical application of LA plasmas. In the majority of experiments on LA trace analysis reported in the literature, only ppm or higher concentration levels were achieved, accompanied by a strong matrix dependence. This is exactly what we observed in determining cobalt in graphite, soil, and steel by using open air LA-LEAFS. However, the optimization of experimental conditions, i.e. using a low pressure argon chamber, a long integration time, and one data acquisition run for all samples in order of increasing admixture concentration, lead to the unique results obtained with metallic matrices. The absence of the matrix effect cannot, however, be generalized with respect to all possible classes of matrices but, as was shown, matrices can certainly be combined into groups for

which a universal calibration procedure, based on of only one set of standards, can be applied.

The spectroscopic usefulness of the technique has been demonstrated in lifetime measurements. This was a first attempt to measure the lifetime of a metastable atomic level by using LA-LEAFS. In the future, the same experimental routine can also be applied for other atomic systems in order to provide valuable spectroscopic information.

The newly developed method of resonance shadow imaging was not, in the direct meaning of the word, LEAFS but it utilized the same principle of selective atomic absorption. Also, laser-induced fluorescence was complementarily used for the measurement of the delay time between the ablating and imaging lasers. Therefore, this method fairly stands among LEAFS applications.

Resonance shadow plasma images were demonstrated to be extremely useful for general understanding of laser plasma evolution. They provided the qualitative information about the neutral species density in the ablation plasma along with the information about the formation and propagation of the laser-induced shock wave. The application of the resonance shadowgraph technique can further elucidate mechanisms of plasma formation and development when different lasers (UV or IR) are used for ablation, as well as can explain pre-breakdown behavior of a light-material system when a laser of moderate power strikes a solid surface. These experiments are currently planned in our laboratory.

APPENDIX A
ACRONYMS USED IN TEXT

AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
CCD	Charge Coupled Device
ETA	Electrothermal Atomization
ICP	Inductively Coupled Plasma
ICCD	Intensified Charge Coupled Device
ID	Isotope Dilution
LA	Laser Ablation
LEAFS	Laser Excited Atomic Fluorescence Spectrometry
LIBS	Laser Induced Breakdown Spectroscopy
LOD	Limit of Detection
MS	Mass Spectrometry
Nd:YAG	Solid state laser on the basis of Yttrium Aluminum Granite doped with Nd
NIST	National Institute of Standards and Technology
PMT	Photomultiplier Tube
RSD	Relative Standard Deviation
SRM	Standard Reference Material
OES	Optical Emission Spectrometry

APPENDIX B
LIST OF RECENT PERSONAL PUBLICATIONS AND MANUSCRIPTS

Presentations

Use of a Furnace with a Graphite Filter for the Determination of Traces of Elements by Laser Excited Atomic Fluorescence Spectrometry, March 5, 1996, Pittsburgh Conference, Chicago, IL.

Excited State Fluorescence of Lead in the Laser Spark, March 18, 1997, Pittsburgh Conference, Atlanta, GA.

Publications and Manuscripts

Use of a Laser-Excited Atomic Fluorescence Spectrometry with a Novel Diffusive Tube Electrothermal Atomizer for the Direct Determination of Silver in Sea Water and in Solid Reference Materials. I.B.Gornushkin, B.W.Smith, J.D.Winefordner, *Spectrochim. Acta B* **51**, 1355 (1996).

A Kinetic Study of The Diffusive Tube Electrothermal Atomizer by Laser Excited Atomic Fluorescence. I.B.Gornushkin, B.W.Smith, J.D.Winefordner, *Spectrochim. Acta B* **51**, 1679 (1996).

Determination of Cobalt in Soil, Steel and Graphite Using Excited State Atomic Fluorescence Induced in a Laser Spark. I.B.Gornushkin, J.E.Kim, B.W.Smith, S.A.Baker, J.D.Winefordner, *Appl. Spectrosc.*, in press.

Determination of Lead in Metallic Reference Materials by Laser Ablation Combined with Laser Excited Atomic Fluorescence. I.B.Gornushkin, S.A.Baker, B.W.Smith, J.D.Winefordner. Submitted, *Spectrochim. Acta B*.

Time-Resolved Shadow Imaging of Laser-Produced Lead and Tin Plasmas. I.B.Gornushkin, M.Clara, B.W.Smith, J.D.Winefordner, R.Neissner, U.Panne. Submitted. *Spectrochim. Acta B*.

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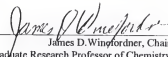
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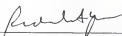
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Igor B. Gornushkin was born in Weimar, Germany, on January 6, 1958. Since 1969 he has lived in St. Petersburg (Russia) where he received his primary and high education. He was graduated from the St. Petersburg State University in 1981 with a major in physics. Then he worked at the Institute of Silicate Chemistry of the Russian Academy of Sciences in the field of analytical chemistry and laser spectroscopy. He entered the University of Florida in the fall of 1993 to pursue his doctoral degree in Prof. Jim Winefordner's group.

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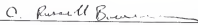
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